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Examination, Evaluation, and Assessment of Tubes Removed from Bruce NGS Unit 1 Steam Generator 3

Report No. 88-20-K

G. Bellamy, F. Gonzalez, and P.J. King
Research Division

Abstract

Five tubes removed from Bruce NGS unit 1 steam generator 3 in January 1987 have been examined by optical and electron microscopy, and analyzed by semiquantitative EDX, ESCA, SAM, and SIMS. Metallurgical analysis showed that the tubing material meets the specifications of ASME standard SB 163 for UNS N06600, and a modified procedure based on the EPRI dual etch suggested that the tubing may have a low susceptibility to stress corrosion cracking. Superficial non-uniform corrosion and intergranular attack to a maximum depth of 10 μm was found in the sludge pile region on all examined tubes; there was no attack above the sludge pile. Analysis of the oxide layer on the area of attack showed some chromium depletion and although this observation is not conclusive, it has been reported in the literature that areas with intergranular attack show such chromium depletion. The observations are consistent with degradation due to the water treatment plant sulphuric acid excursion of 1986 01 18. A large proportion of tubes in all Bruce NGS-A steam generators may have suffered localized corrosion to a similar extent. Although deposits remaining on the tube surfaces were thin, the extent of the sludge pile was discernible by a darker oxide and deposit band. Deposits in the sludge pile region contained high concentrations of sulphate that may be related to the acid incident. Both sulphate and chloride levels were higher than those found in previous analyses [unit 3 steam generator 3]. Copper-rich deposits, present in some areas, may have contributed to the observed attack. Conversely, the presence of complex silicates may have had a mitigating effect on the rate of degradation. Attack was undetected by either eddy current or ultrasonic inspection; thus demonstrating the importance of tube removal to detect corrosion in the early stages.

job	file	date	report no.
740636-173-552	836.3332 x823.424, x827.27	March 31, 1988	88-20-K

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To: B. Montford
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EXAMINATION, EVALUATION, AND ASSESSMENT OF TUBES REMOVED FROM BRUCE NGS UNIT 1 STEAM GENERATOR 3

G. Bellamy, F. Gonzalez, and P.J. King
Research Division

INTRODUCTION

Units 1 to 4 at Bruce NGS experienced a water treatment plant acid excursion on 1986 01 18. Although the cause was remedied within 72 hours, no action was taken to remove accumulated sulphuric acid from the sludge pile in the steam generators. At the time of the incident Research Division staff identified possible corrosion consequences as wastage, pitting, or intergranular attack of tubing in creviced and deposit covered regions. The crux of the discussion was that corrosion damage may have occurred within the period of the actual excursion, and that it could continue if the acid was not effectively removed from the steam generators. Remedial action was later taken by the station based on the recommendations of Chemistry and Metallurgy, CNS, staff; but only on Unit 3, which was shut down for a hot soak on 1986 01 24.

Non-destructive inspections were performed and 5 tube sections were removed from the tubesheet region of steam generator 3 during the fall 1986 outage of Unit 1. Evaluations of tubing condition were carried out principally on tube R58-S42, in accordance with a plan drawn up by G. Curcio [memo to distribution 87 03 31, file NCCM-BGA-33110]. The investigations involved three tasks as listed below.

TASK	INVESTIGATOR		ATTACHMENT
Metallographic Examination	G. Bellamy,	Metallurgical Research	A
Tube Deposit Analyses	F. Gonzalez,	Chemical Research	B
Corrosion Assessment	P. King,	Metallurgical Research	C

This report summarizes the results of all evaluations. The attached individual reports present in detail the findings of the individual investigations. Information about the variability of measured quantities and confidence in the generalization of results is improved by the use of multiple samples. However, the investigations were limited by sample allocation, thereby making generalizations difficult. This should be borne in mind when reviewing the information provided.

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EVALUATIONS UNDERTAKEN

Several procedures were used to determine the metallurgical condition of the tubing, examine the outside surfaces for evidence of corrosion degradation, and to determine the physical and chemical characteristics of tube deposits.

Detailed visual examination of as-received tubes was part of all three tasks; the unaided eye and low power stereo microscopy were employed to complete this part of the work.

Standard metallographic and microscopic procedures were employed for the majority of the metallurgical and corrosion evaluations. Scanning electron microscopy was used to reveal detail of cross-sections and surface features. Carbide distribution was examined by means of the EPRI dual-etch method which sequentially reveals carbide and grain boundary locations. An assessment of the carbide distribution may provide some indication of the susceptibility of the tubing to stress corrosion cracking. Depth of attack was estimated by measurements on cross sections and by refocussing measurements with an optical microscope having a calibrated focus adjustment.

Spectroscopic analytical techniques were used to obtain chemical information because of their surface sensitive nature and their non-destructive characteristics. Various techniques were used, as listed below, since they provide complementary and confirmatory evidence.

ESCA	Electron Spectroscopy for Chemical Analysis
SIMS	Secondary Ion Mass Spectroscopy
EDXA	Energy Dispersive X-ray Analysis
SAM	Scanning Auger Microscopy

OBSERVATIONS AND INFORMATION OBTAINED

Figure 1 summarizes the results of the initial visual examination. It shows the general condition of received samples and the locations of the principal features: rolled joint, sludge pile, other deposits, and corrosion damage.

The metallurgical investigation showed that the tubing material meets the specifications of ASME standard SB163 for UNS N06600. The tubes had been plastically deformed during tube removal, and gauging indicated a reduction in wall thickness and diameter of 3 to 5%. It was found that the standard EPRI dual etch was not useful because of the extent of cold plastic deformation; a modified etch suggested that the tubing may have a low susceptibility to stress corrosion cracking.

All investigations indicated localized corrosion of tubing under the sludge pile. A metallurgical cross-section showed intergranular and twin boundary attack to a depth of 5 μm. The corrosion assessment added to this by further identifying the corrosion as non–uniform general attack throughout most of the sludge region. Intergranular attack was evident only at the tube-tubesheet crevice region. The intergranular attack and some general dissolution in this area had produced wide grain boundary grooves to about one-half grain depth. The maximum measured depth of attack obtained by refocussing was 10 μm, in good agreement with the depth measured on the metallurgical cross-section.

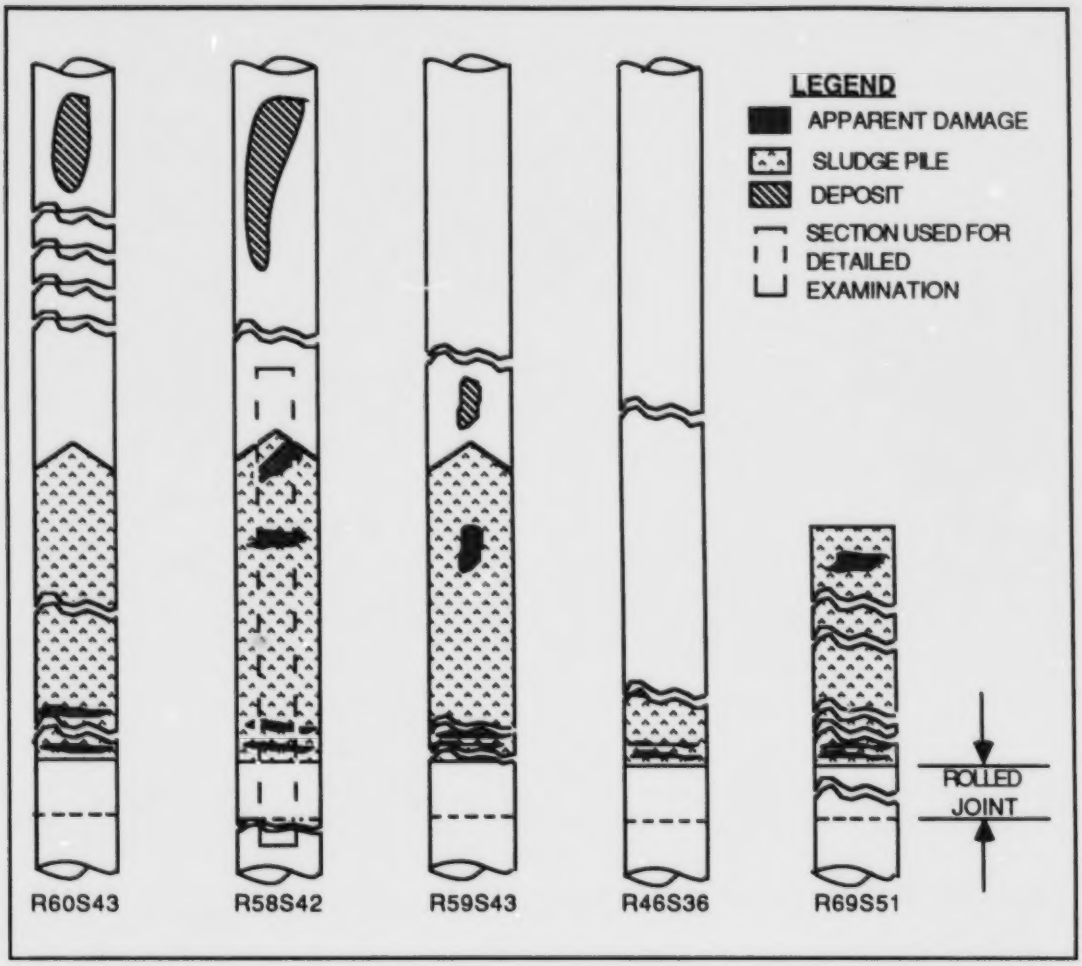
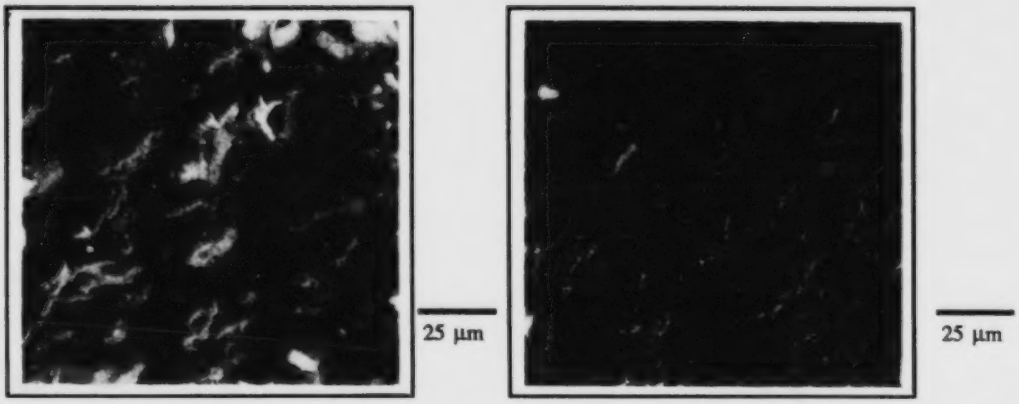


Figure 1. General visual appearance of tubes from Bruce NGS Unit 1, steam generator 3. Note the numerous breaks on most tubes. In all cases, corrosion was evident at the tube-tubesheet crevice region just above the rolled joint. Detailed analyses were confined to the regions identified on tube R58–S42.

Figure 2 shows the morphological features of the corrosion damage. These features, listed below, are consistent with sulphuric acid attack of alloy N06600.

- shallow, non-uniform corrosion
- regions of polishing and etching, suggesting the presence during corrosion of a film of concentrated solution at the metal surface



a] At the tube-tubesheet crevice region showing detail of the wide grain boundary grooves produced by intergranular attack and some general dissolution.

b] Within the lower part of the sludge pile showing non-uniform corrosion. The corrosion has resulted in grains with a polished appearance outlined by shallow boundary grooving.

Figure 2. Appearance of corrosion damage in sludge pile region of Bruce NGS Unit 1, SG 3 tube R58–S42. The morphological features identified are consistent with sulphuric acid attack.

- intergranular attack
- general lack of crystallographic facets [that would be more typical of active dissolution in the absence of a solution film]

Deposits were generally extremely thin resulting in strong contributions from the underlying metal in many of the analyses. Even so, extensive chemical information was obtained. Many analyses were performed by the various techniques. These are representative of only small local areas of the surface of one tube; therefore,the validity of generalization to other tubes is unknown. The combination of techniques yielded the following information.

Sulphur: High sulphur concentrations were found in the sludge and other tube deposits. It is present principally as sulphate, but some sulphite was also identified in deposits away from the sludge pile. The origin of the sulphite is not clear; it may have formed during the excursion but also during sampling. The absence of reduced sulphur species in previous Bruce NGS A steam generator deposits means that sulphite formation during normal operation is unlikely. Sulphur was also incorporated into the oxide layer on the tubing.

Chlorine: Chlorine, present as chloride, was found in high concentrations in the sludge; somewhat lower concentrations were found in other tube deposits. Chlorine was also incorporated into the tube oxide.

Chromium: A general oxide surface enrichment of chromium was identified on unattacked metal surfaces. A possible oxide surface depletion of chromium was noted in the attacked region, but no statistical significance could be assigned to the observation since it was limited to only one sample.

Copper: Copper was found in significant quantities on tube surfaces, including those directly adjacent to some regions of attack. Copper was present in both the cupric and cuprous as well as the metallic state.

Other elements: The metals magnesium, aluminum, calcium, silicon, potassium, and sodium were all present in significant quantities in tube deposits. Possible relationships were identified for groups of these elements. Lithium was found by SIMS to be present in trace quantities.

PRINCIPAL CONCLUSIONS

The most significant conclusion arising from the three investigations is that the observed corrosion was caused by the water treatment plant acid excursion of 1986 01 18. The propagation period is unknown; however, it may not have been limited to the duration of the excursion and could have continued until the Fall 1986 outage. Copper [copper ion reduction] may have contributed directly to the observed attack while the presence of complex silicates may have had a counteracting effect on the rate of tube attack. Comparable corrosion damage had not been seen in other Bruce NGS A units prior to the acid excursion; none was found on tubing removed from the sludge pile region of a unit 3 steam generator, nor was any found in the creviced regions of U-bend tubes removed from other Bruce NGS A units.

The other major conclusions are listed below.

Statistically, at a 95% confidence level, at least 55% of tubes creviced by deposits have suffered localized corrosion in Bruce NGS Unit 1, steam generator 3. There is a significant probability that a very high proportion of such tubes have been attacked to some extent.

The sludge pile is non-protective; it and other crevice forming deposits pose a substantial danger to tubing integrity. Sulphur and chlorine in the sludge were at significantly higher concentrations than in previous analyses. High sulphur is consistent with the acid excursion of January 1986. Sulphite was identified in deposits away from the sludge pile. A conclusive explanation for its origin cannot be advanced; however, its presence could be deleterious.

Steam generators of the other 3 units of Bruce A station are likely to have suffered attack. This attack may be more or less severe than that observed on unit 1. Neither the effects of different recorded unit chemistries nor the influence of the hot soak are predictable based on the results of these examinations.

The tubing microstructure indicates that its stress corrosion cracking susceptibility is probably low

Too few samples were allotted to generate statistical confidence in the generalization of the results to other tubes.

RECOMMENDATIONS

Three recommendations are advanced as a result of this work.

1] Additional samples should be obtained from this and other units to confirm the predicted extent of damage and the presence of reduced sulphur species.

2] It is essential to include tube removal in future steam generator inspections.

3] Ultrasonic or eddy current methods should be developed for improved detectability of very shallow attack, discrimination of attack morphology, and quantification of dimensions.

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METALLOGRAPHIC EXAMINATION OF SG TUBING EXPOSED TO A SULPHURIC ACID EXCURSION BOILER 3 - UNIT 1 - BNGS 'A'

G. Bellamy

Inconel alloy 600 steam generator tubing exposed to the low pH conditions associated with a sulphuric acid excursion suffered OD surface intergranular and twin boundary attack to a maximum depth of 0.005 mm or 0.48% of wall. Attack was confined to crevice regions either beneath the sludge pile or between the upper rolled joint and the top face of the tube sheet. An EPRI recommended orthophosphoric acid etching technique for determination of susceptibility to intergranular stress corrosion cracking is useful only on tubing which has suffered little or no cold plastic deformation during removal from the steam generator. A modified etching procedure produced results indicative of minimal susceptibility to intergranular stress corrosion cracking in service.

INTRODUCTION

Research report M85-5-K presented early findings in a continuing periodic inspection program designed to provide early warning of steam generator tube OD surface in-service degradation. The area of particular concern is beneath the sludge pile and between the upper rolled joint and the top face of the tube sheet; ie zones particularly susceptible to crevice corrosion during periods of less than optimal boiler water contaminant control. Problems would be most likely to occur in this region on the hot leg side of the U-bent tube.

As part of the continuing program susceptible areas of tubes R46-S36, R58-S42, R59-S43, R60-S43, and R69-S51 were removed and shipped to the Research Division for examination.

Analysis of surface deposits is being conducted by the Chemical Research Department and the Corrosion and Tritium Technology Section will report on OD surface topography. This report is concerned only with tube gauging, material composition and metallography.

During a preliminary visual and low power stereoscopic examination it was decided that the most useful information could be had from tube R58-S42. The rest were archived.

The aforementioned preliminary OD surface examination disclosed two lightly etched areas indicative of in-service corrosive attack. One was from an area immediately below the upper surface of the sludge pile and the other from within the tube sheet crevice immediately above the upper rolled joint. Following tube gauging, 20 mm long x 5 mm wide strips were removed for a detailed metallographic study of the etching phenomenon.

Gauging

At the request of CNS personnel tube OD dimensions were measured on two mutually perpendicular axes in the as-received condition, ie surface deposits were not removed. Measurements were taken at 25 mm intervals starting at the bottom. Table 1 compares results with specified tolerances for new tubing.

Tube wall thickness measurements were taken from photographs of transverse sections. These appear as Figures 1e, 3d and 5e for the following areas:

	Area	Total Wall Thickness (mm)
1.	Immediately above the upper rolled joint	1.04
2.	Immediately below the upper surface of the sludge pile	1.08
3.	Immediately above the sludge pile	1.10

The specified nominal wall thickness for new tubing is: 1.12 mm.

Chemical Analyses

A sample of tube R58-S42 material was submitted to the Chemical Research Department together with a request for compositional analysis. Table 2 compares results obtained with requirements of the purchase specification.

Metallography

The 20 mm long strips selected for detailed metallographic examination were mounted and prepared to reveal microstructural detail in a through wall longitudinal plane.

Primary attention was focussed upon OD surface conditions. A comparison was made between crevice areas where evidence of etching had been observed and non-creviced regions above the top of the sludge pile. For purposes of comparison an archived unused sample was examined. This was produced using the same mill processes as tube R58-S42 but it had not been exposed to any service environment.

Figures 1, 3 and 5 compare microstructure and surface conditions in the three areas of interest on tube R58-S42. This evidence was obtained using light microscopy on samples electrolytically etched in a 10 wt% aqueous solution of oxalic acid for 5 seconds at a potential of 6 volts with a type 304 stainless steel cathode. Some evidence of slight intergranular OD surface attack is seen in Figures 1c and 3c. These illustrations represent the worst areas of the rolled joint and sludge pile crevices respectively. Elsewhere except for some minor mechanical removal damage OD surfaces were smooth and essentially unattacked as noted in Figures 1a and b, 3a and 5 b and c.

Figures 1d and e, 3b and d and 5d and e show through wall sections in longitudinal and transverse planes respectively. Measurements taken in the transverse plane will yield accurate assessments of wall thickness in the regions of interest.

General microstructural features of the post-service tubing are most clearly resolved in Figures 1a and particularly 3c as discrete globular grain boundary carbide precipitates in a twinned equiaxed austenitic matrix. A very light dispersion of small globular carbides is also visible within the grains.

Considering the very superficial nature of intergranular attack in the tube OD creviced areas, a further examination was conducted using the superior resolution of the scanning electron microscope. The most severely attacked regions are seen in Figures 7c, 7d, 8c and 8d with less severely attacked zones typified in Figures 7b and 8b. A comparison with the archived, unused tube OD surface is afforded by the inclusion of Figure 10. The smooth unattacked surface in Figure 10 compares favourably with essentially similar features from the OD surface of tube R46-S36 from which was obtained a sample from the non-wetted in-service area between the tube sheet upper and lower rolled joints. Details of the R46-S36 tube OD surface appear in Figure 9.

Arrows in Figures 5a, 7a and 8a indicate on a macro-scale areas of the 8 mm long strips of tube R58-S42 material showing the worst corrosive attack which in the case of the areas illustrated throughout Figure 5 was essentially zero.

General microstructural features revealed by Figures 7 and 8 are similar to those discussed earlier. At the very high magnifications of Figures 7d and 8d it is clear that both grain boundaries and twin boundaries have suffered corrosive attack to the same extent.

At the specific request of CNS personnel metallographic sections from the creviced areas and the area above the sludge pile in tube R58-S42 were subjected to a dual etching technique recommended by EPRI for determining relative susceptibility to in-service intergranular stress corrosion cracking. By correlation with service experience EPRI claim that an acceptable microstructure with minimal susceptibility to stress corrosion cracking is one having substantial grain boundary carbide precipitation and only modest carbide precipitation within the grains. They further emphasize that there must be no evidence of carbide denudation in the immediate vicinity of grain boundaries. Figures 2, 4 and 6 document results of applying the EPRI recommended procedures to areas of interest on tube R58-S42. Figures 2a, 4a and 6a show grain boundaries and other microstructural features as revealed by electrolytically etching the suitably prepared specimens for 30 seconds at a potential relative to a type 304 stainless steel cathode of 3 volts in a 5 vol % solution of nitric acid in methanol.

Following removal of this etch the samples were re-etched using a procedure designed specifically to emphasize carbide distribution in the same areas illustrated in Figures 2a, 4a and 6a. The second electrolytic etching procedure utilised the same equipment and electrical conditions as before but substituted an 89 vol % solution of orthophosphoric acid in water for the previously used nital solution. Results in Figures 2c, 4c and 6c show heavy masking of other microstructural features by strain lines indicative of prior substantial cold deformation. In an attempt to suppress development of the strain lines the etching process was repeated for a reduced time, ie 5 seconds instead of the 15 to 30 recommended by EPRI. Figures 2b, 4b and 6b show that this technique was moderately successful. Figure 2b in particular shows the same overall carbide distribution as that described earlier for Figures 1a and 3c. Of particular interest in Figure 2b is the complete grain boundary definition, modest concentration of globular carbides within grains and no evidence of carbide denudation adjacent to grains; ie the microstructure is acceptable and represents a condition of minimum susceptibility to intergranular stress corrosion cracking.

To conclude the metallographic examination of recently removed Inconel alloy 600 steam generator tubes, Research Division were asked to examine an OD surface area of tube R46-S36 from which had emanated an ultrasonic inspection signal.

Stereoscopic examination of the OD surface area revealed the oxide filled cavity arrowed in Figure 11a. Longitudinal sectioning disclosed the irregular OD surface profile of Figure 11b associated with the cavity near the top left corner of the illustration. High resolution scanning electron microscopy on the etched longitudinal section resolved detail appearing as Figures 11c and d. Both show an oxide filled OD surface depression approximately 0.1 mm deep. Figure 11d indicates that the depression was formed by cold mechanical deformation of the microstructure. Remote from the immediate vicinity of the depression the tubing material general microstructure consists of the equiaxed grain boundary carbide decorated austenite seen in the lower half of Figure 11c.

DISCUSSION AND CONCLUSIONS

1. Following in-service exposure to a low pH sulphuric acid excursion steam generator tube R58-S42 shows in both upper rolled joint and sludge pile creviced regions OD surface intergranular and twin boundary corrosive attack to a depth of 0.005 mm or 0.48% of wall. The tubing material composition is within limits set by ASME specification SB163 for alloy UNS N06600.

2. Modification of an EPRI recommended dual etching technique produced results indicating that the microstructural condition of Inconel alloy 600 tube R58-S42 has minimal susceptibility to intergranular stress corrosion cracking during normal steam generator service conditions.

3. The standard EPRI recommended dual etching procedure is useful only on tubing which has suffered little or no cold plastic deformation during removal from the steam generator. Results from other workers emphasize the important role of grain boundary sensitization by carbide precipitation and resultant formation of a chromium depleted zone in rendering Inconel alloy 600 susceptible to both stress corrosion cracking and intergranular attack. Since the EPRI etching procedure does not detect this condition its value appears to be minimal in investigations of the current type.

4. An ultrasonic test indication from the OD surface of Inconel alloy tube R46-S36 emanated from an area in which oxides had been pressed into the surface producing by cold mechanical deformation an appoximately 0.1 mm deep depression.

ACKNOWLEDGEMENT

Gauging and metallographic services were provided by Mr. F.W. Smith.

TABLE 1

OD GAUGING OF AS-RECEIVED TUBE R58-S42

Distance from Bottom End (mm)	Tube Outer Diameter (mm) Axis A	Axis B
0	12.92	13.15
25	13.14	13.14
50	12.52	12.58
75	12.57	12.53
100	12.61	12.64
125	12.47	12.26
150	12.52	12.47
175	12.10	12.32
200	12.55	12.54
225	12.62	12.55
250	12.68	12.60
275	12.57	12.44
300	12.59	12.54
325	12.28	12.58
350	12.57	12.52
375	12.63	12.50
400	12.60	12.49
425	12.55	12.52
450	12.65	12.46
475	12.72	12.50
500	12.59	12.41
525	12.64	12.36
550	12.63	12.33
575	12.62	12.36
600	12.70	12.27
625	12.59	12.37
650	12.49	12.38
675	12.52	12.29

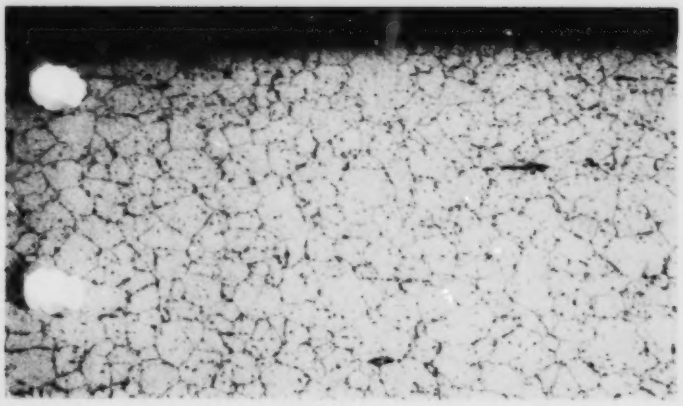
OD tolerance on unused tubing is 12.96 mm +0.13 mm
-0.00 mm

TABLE 2

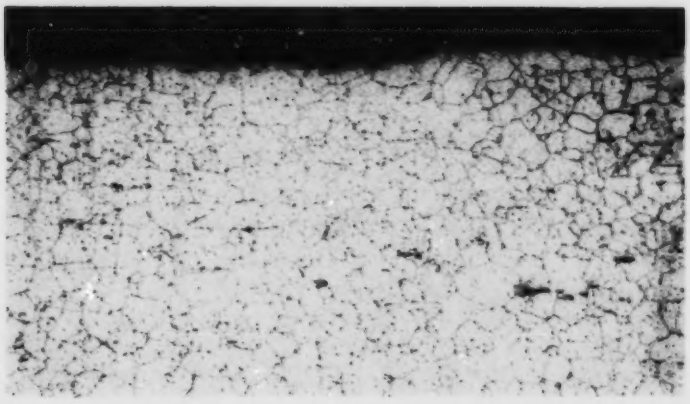
CHEMICAL ANALYSES

Sample	Element - wt * % Concentration							
	C	Mn	Si	S	Ni	Cu	Fe	Cr
Tube R58-S42	0.05	0.25	0.2	0.007	76.7	0.1	5.76	14.7
ASME spec SB 163 alloy UNS N06600	0.15 max	1.0 max	0.5 max	0.015 max	72.0 min	0.5 max	6.0-10.0	14.0-17.0

*Chemical Research Dept Report CE87-0907-K



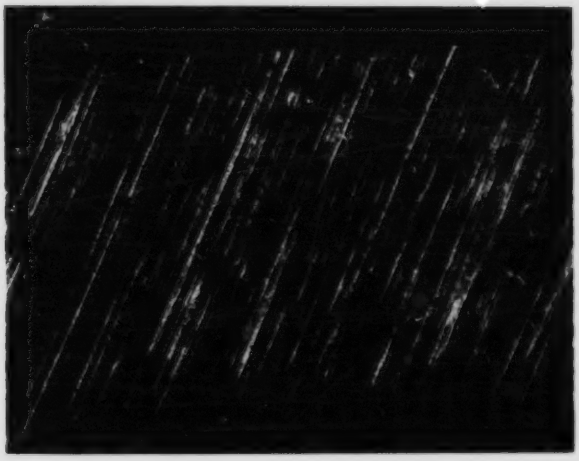
a) X 200 mag



b) X 200 mag

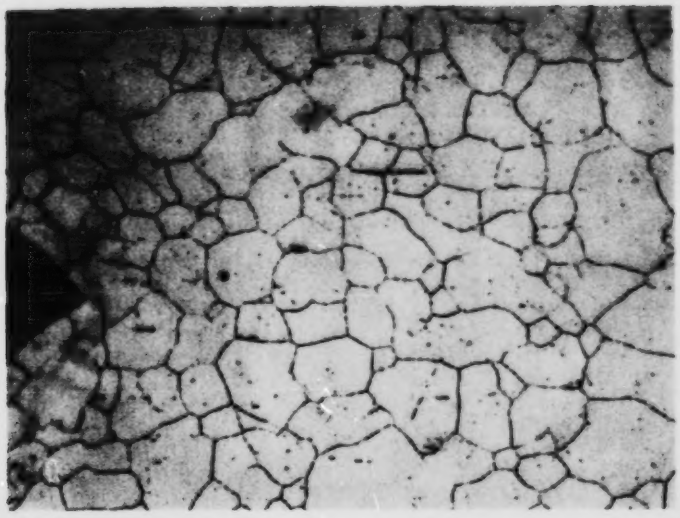
c) X 200 mag

d) X 50 mag



e) X 50 mag

FIGURE 1 - TUBE R58-S42 IMMEDIATELY ABOVE THE UPPER ROLLED JOINT-SURFACE CORROSION



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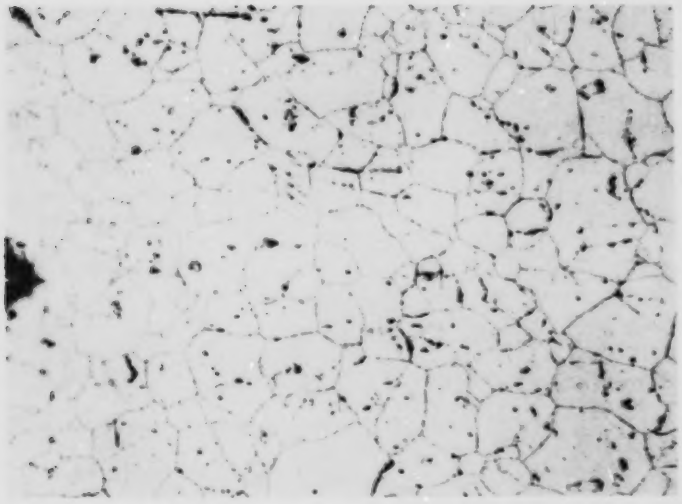

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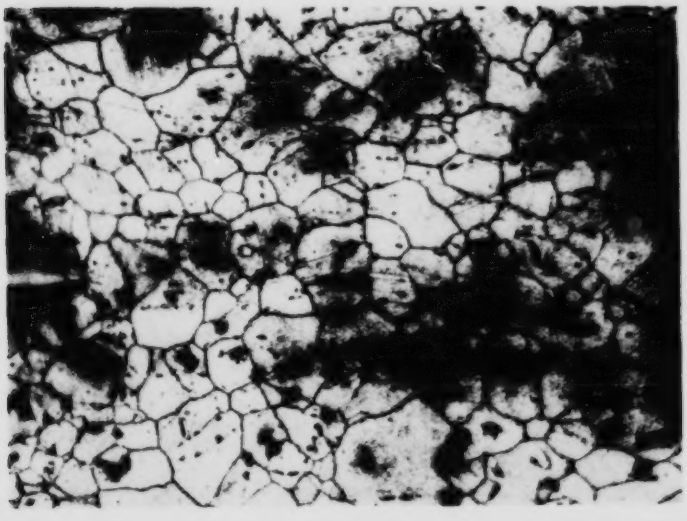
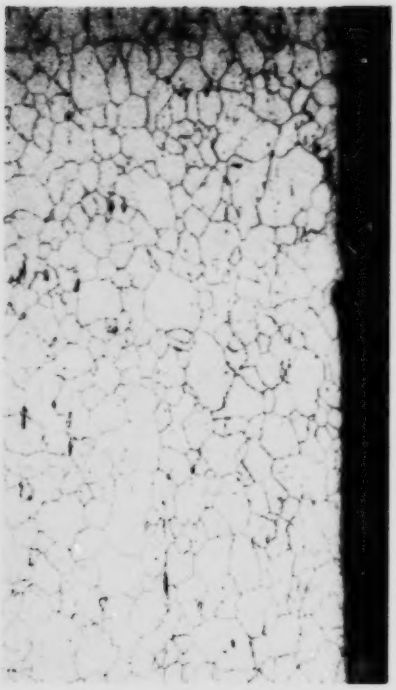


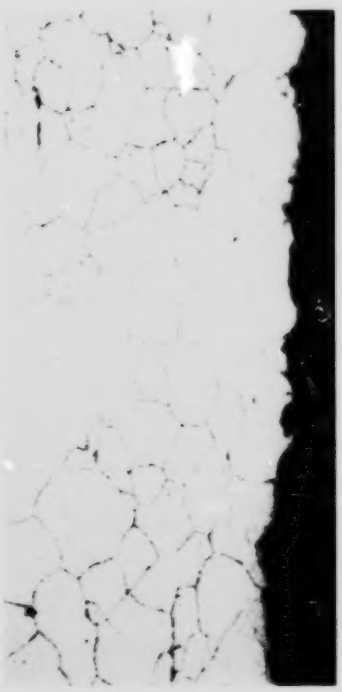
c)

FIGURE 2 - TUBE R58-S42 IMMEDIATELY ABOVE THE UPPER ROLLED JOINT - MICROSTRUCTURAL FEATURES, X 400 mag

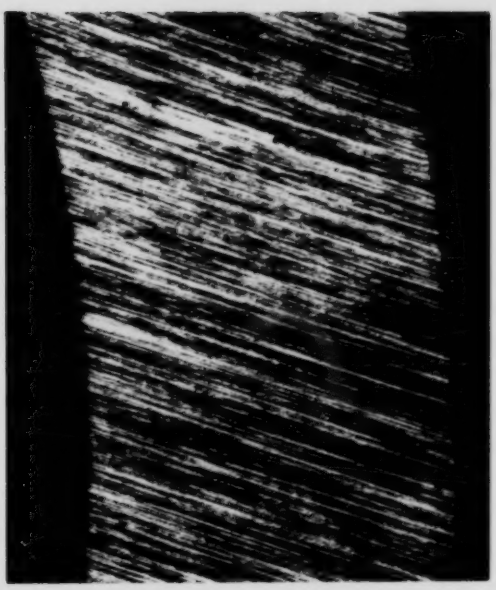


a) X 200 mag

b) X 50 mag

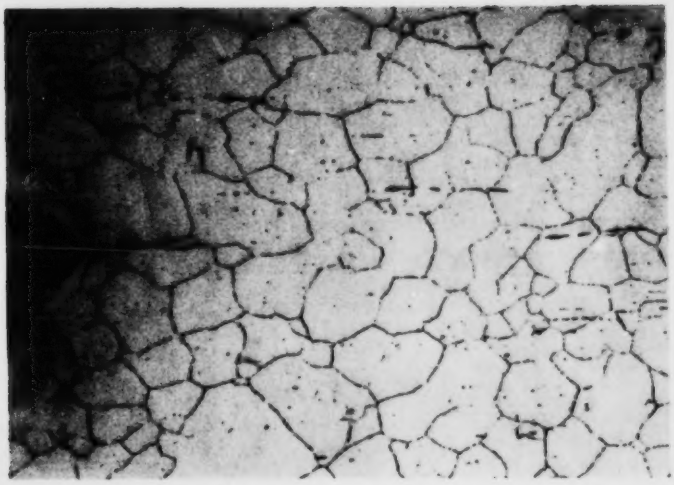


c) X 400 mag

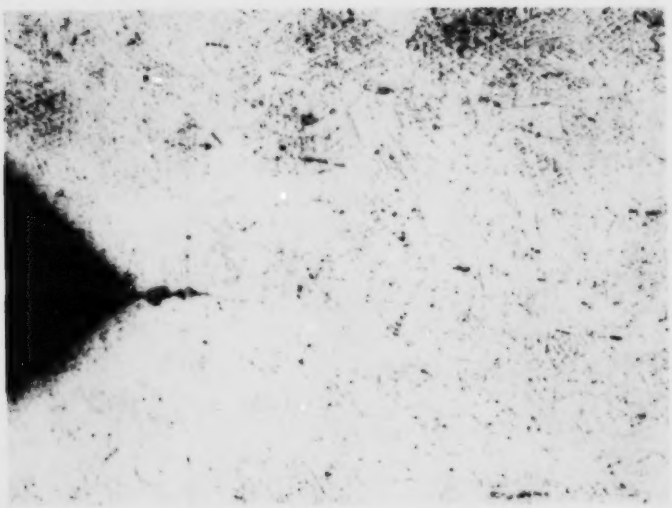


d) X 50 mag

FIGURE 3 - TUBE R58-S42 IMMEDIATELY BELOW THE UPPER SURFACE OF THE SLUDGE PILE-SURFACE CORROSION



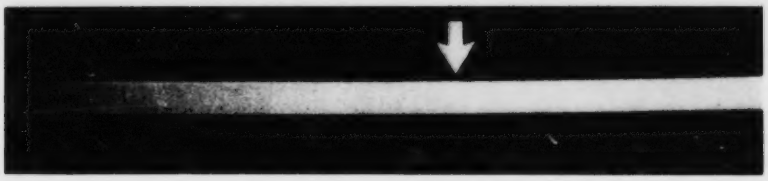
a)



b)

c)

FIGURE 4 - TUBE R58-S42 IMMEDIATELY BELOW THE UPPER SURFACE OF THE SLUDGE PILE-MICROSTRUCTURAL FEATURES, X 400 mag



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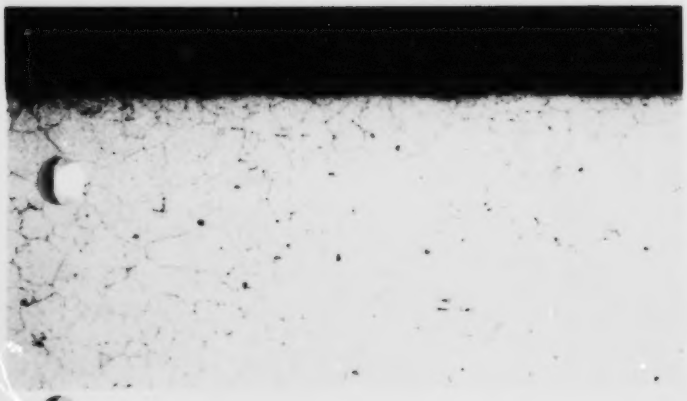

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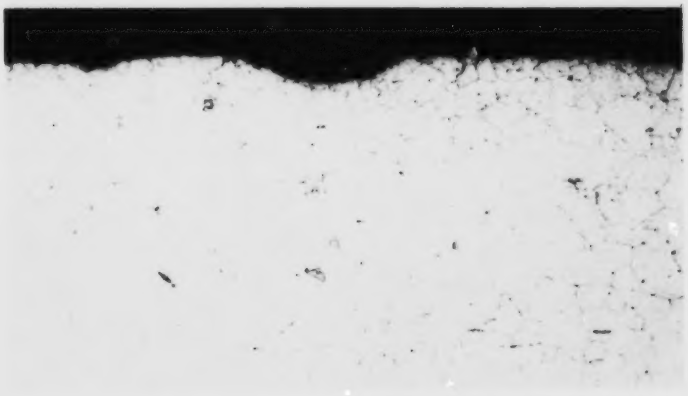
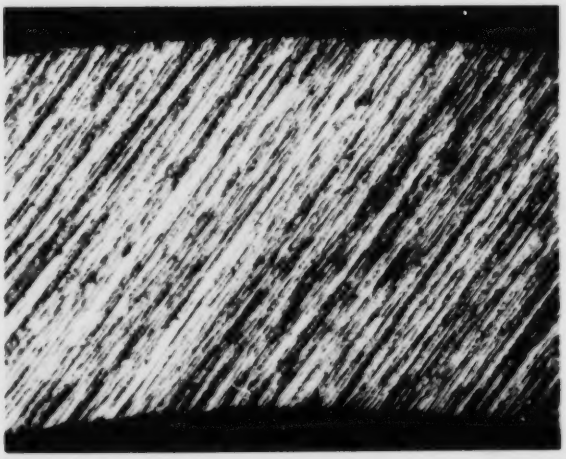


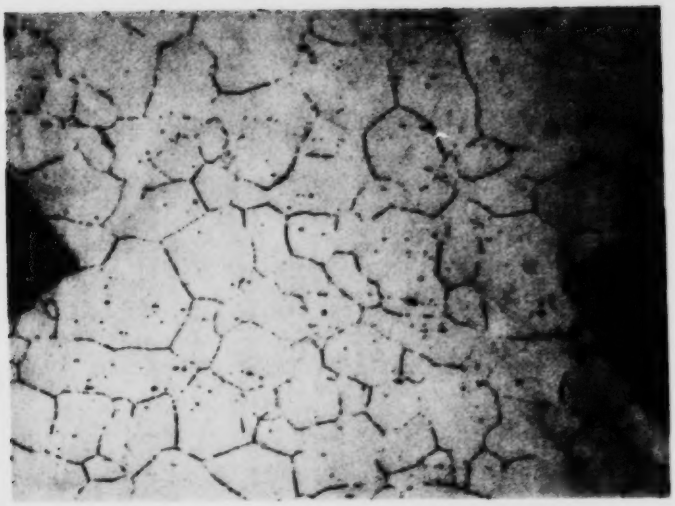
c) X 200 mag

d) X 50 mag



e) X 50 mag

FIGURE 5 - TUBE R58-S42 IMMEDIATELY ABOVE THE SLUDGE PILE - SURFACE CORROSION



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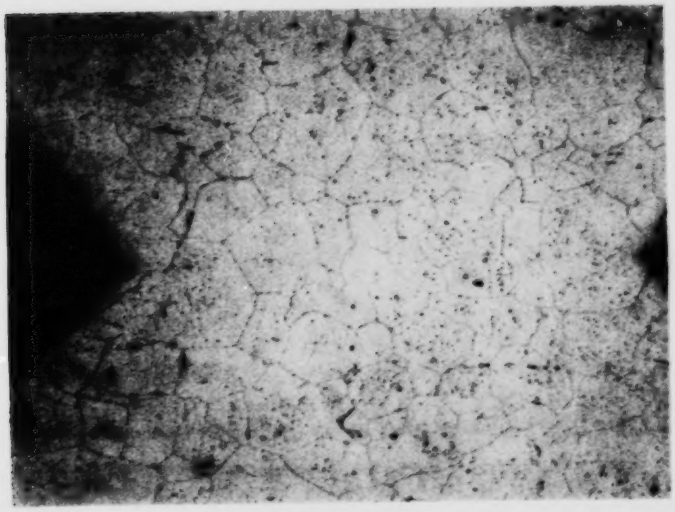
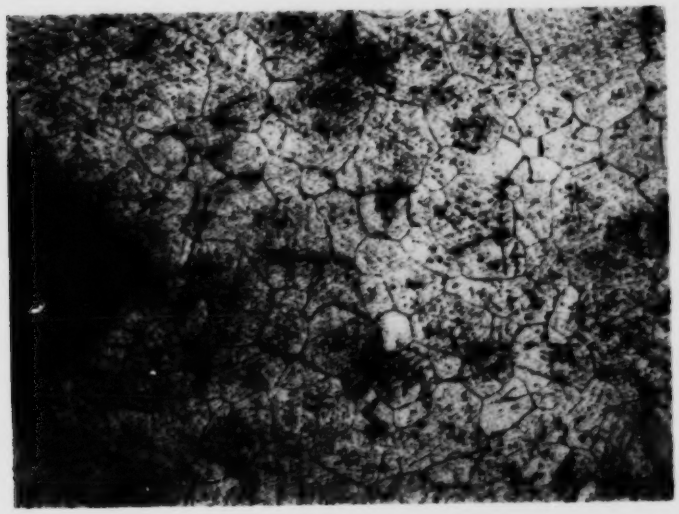
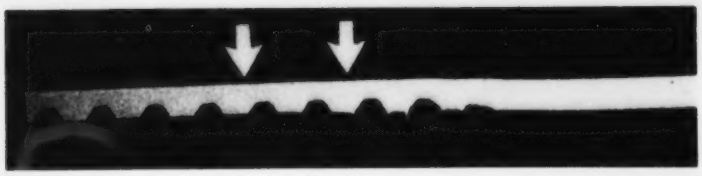


b)



c)

FIGURE 6 - TUBE R58-S42 IMMEDIATELY ABOVE THE SLUDGE PILE - MICROSTRUCTURAL FEATURES, X 400 mag



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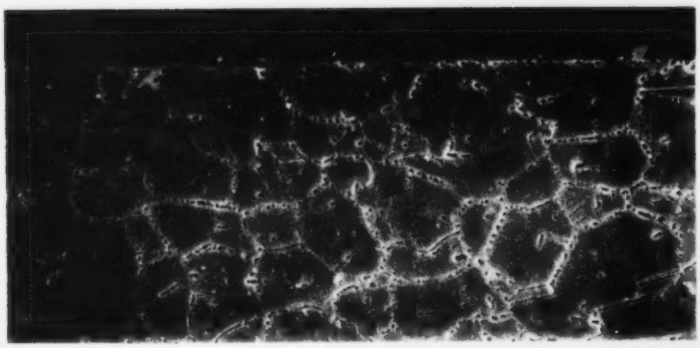

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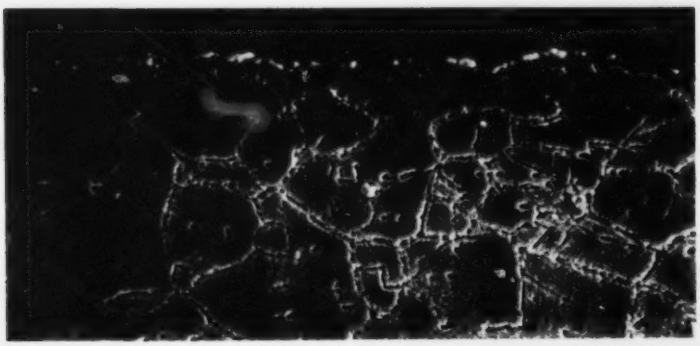

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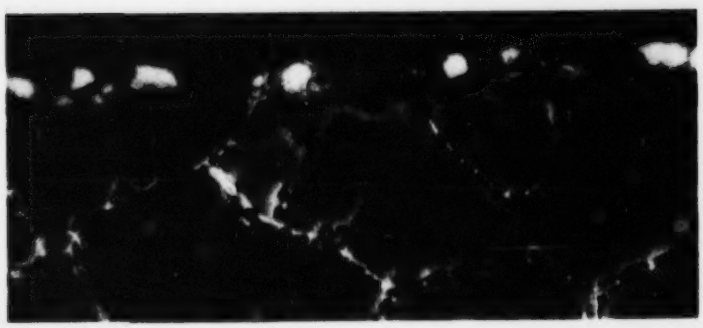
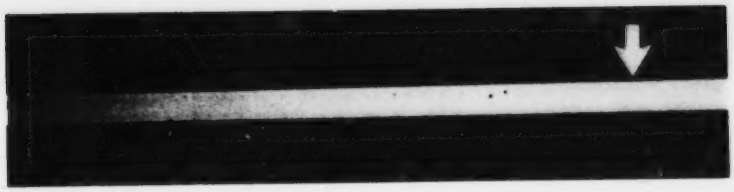


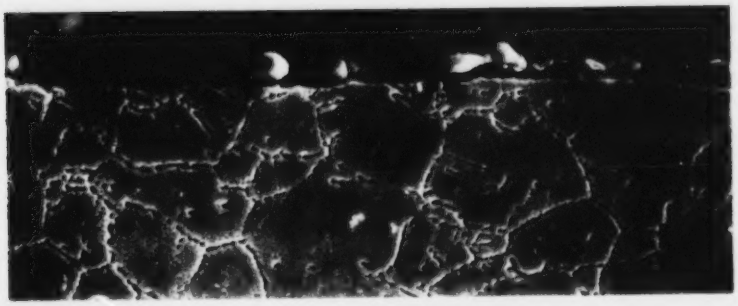
d) X 2400 mag

FIGURE 7 - TUBE R58-S42 IMMEDIATELY ABOVE THE UPPER ROLLED JOINT - SURFACE CORROSION

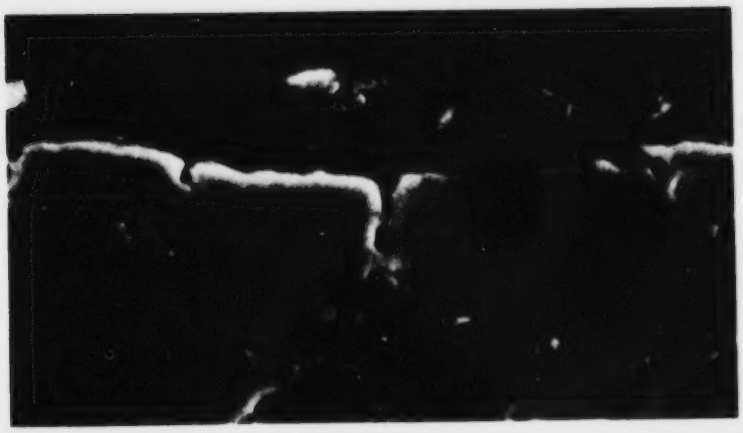


a) X 5 mag

b) X 660 mag



c) X 660 mag

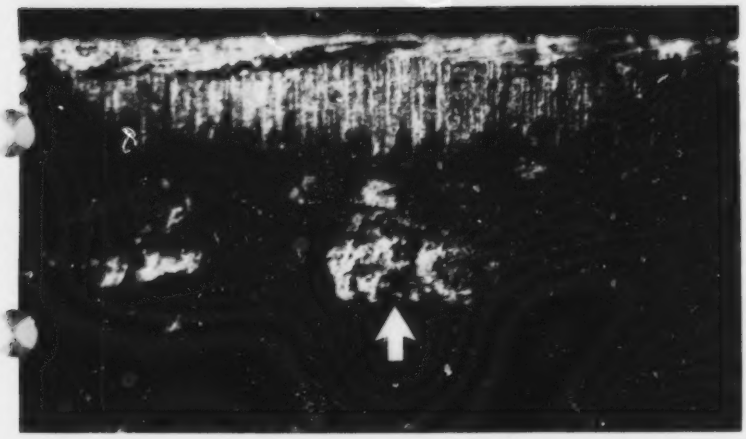


d) X 2400 mag

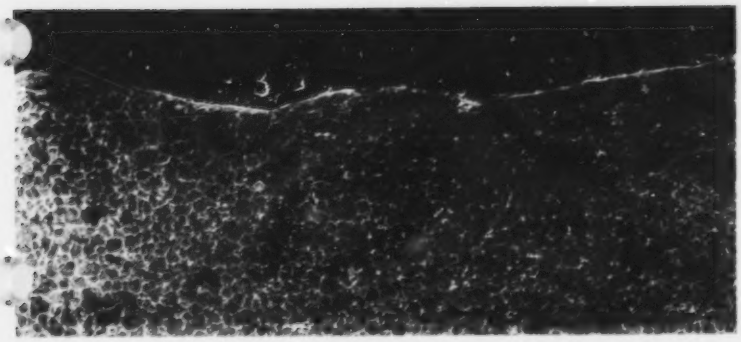
FIGURE 8 - TUBE R58-S42 IMMEDIATELY BELOW THE UPPER SURFACE OF THE SLUDGE PILE - SURFACE CORROSION

FIGURE 9 - TUBE R46 S36 BETWEEN THE UPPER & LOWER ROLLED JOINTS, X 660 mag

FIGURE 10 - UNUSED TUBING OD SURFACE CONDITION, X 660 mag



a) X 30 mag



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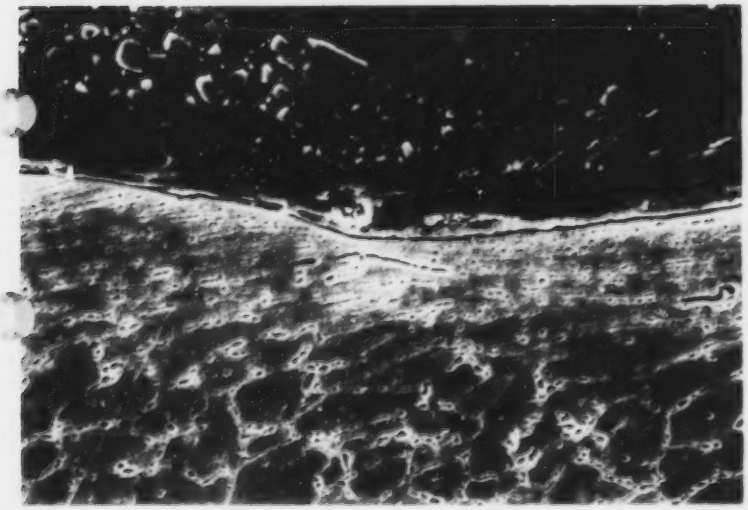
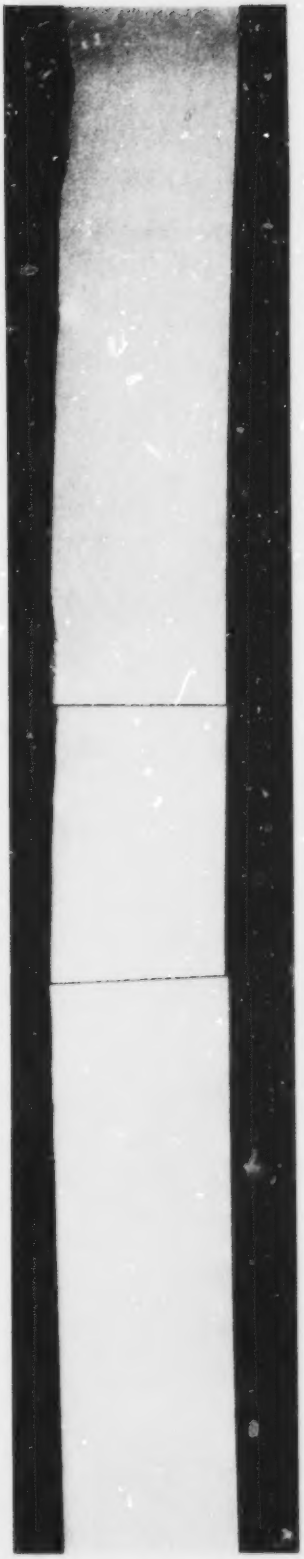


d) X 650 mag



b) X 24 mag

FIGURE 11 - ULTRASONIC INDICATION AREA ON TUBE R46-S36

ANALYSIS OF BRUCE NGS "A" UNIT 1 STEAM GENERATOR 3 TUBE DEPOSITS

F. Gonzalez
Corrosion Chemistry and Decontamination
Project Group
Chemical Research Department

ABSTRACT

The secondary side deposits of tubes sampled from the tubesheet region of unit 1, steam generator 3 were analyzed. Each tube showed surface attack in areas which were originally under the sludge pile. The deposits on this region contained high concentrations of sulphate and chloride. The high sulphate concentrations may be related to a sulphuric acid excursion in January 1986. The oxide layer on the area of attack showed some indication of chromium depletion which is symptomatic of intergranular attack on Inconel 600. Some of the tube damage may be related to the localized presence of copper-rich deposits. Sulphite was the only reduced sulphur species identified in the deposits. Its origin is not clear. The presence of complex silicates among the corrosion products may have had some mitigating effect on the rate of tube attack. It is recommended that additional samples be obtained from this and other units to determine the present rate of the tube material attack and the extent of damage in other units. The presence of reduced sulphur species and the chemistry of the oxide layer on the areas of attack should be confirmed.

EXTENDED SUMMARY

ANALYSIS OF BRUCE NGS "A" UNIT 1 STEAM GENERATOR 3 TUBE DEPOSITS

F. Gonzalez

In January 1986, there was a sulphuric acid in-leakage incident in the make-up water system of Bruce NGS "A". The acid reached the steam generators and the pH of the boiler water went out of specifications. To assess possible damage to the steam generator tubes, five tube sections from the tubesheet region of steam generator 3 in unit 1 were sampled. The objective of this project was to examine, analyze and characterize the surface deposits of the tube samples.

The tube samples were examined by optical and electron microscopy. Semiquantitative EDX analysis was carried out most areas of interest. Some selected areas were also analyzed by ESCA, SAM and SIMS.

Because of the sampling technique used the deposits left on the tube surfaces were very thin although thicker deposits were preserved in localized areas. Each tube had a sludge pile mark characterized by the presence of darker oxide/deposits. Each tube had areas of surface attack which were originally under the sludge pile region. Many of these regions were near the tubesheet surface.

The deposits on the sludge pile region contained concentrations of sulphate and chloride higher than those found in previous analyses (unit 3 steam generator 3). The higher concentrations of sulphate may be related to the acid incident. Analysis of the oxide layer on the area of attack showed some chromium depletion although this conclusion can only be made tentative. It has been reported in the literature that areas with IGA attack show chromium depletion on the external oxide film.

Copper-rich deposits were present in some areas. Cupric and cuprous oxide were detected on the surface of these deposits but the oxide layers were thin and most of the deposit was metallic

copper. Some tube damage may be related to the presence of the copper deposits. The electrochemical potential under the sludge pile was likely to be quite aggressive.

Sulphite was identified in deposits away from the sludge pile. It may have been formed during the acid excursion but also during sampling. Complex silicates are present among the corrosion products. This presence may have some mitigating effect on the rate of tube attack.

It is recommended that additional samples be obtained from this and other units to determine the present rate of the tube material attack and the extent of damage in other units. The presence of reduced sulphur species and the chemistry of the oxide layer on the areas of attack should be confirmed.

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ANALYSIS OF BRUCE NGS UNIT 1
STEAM GENERATOR 3 TUBE DEPOSITS

1.0 INTRODUCTION

In January 1986, there was a sulphuric acid in-leakage incident in the make-up water system of Bruce A NGS. The acid reached the steam generators and the pH of the boiler water went out of specifications. To assess possible damage to the steam generator tubes, five tube samples from the tubesheet region of unit 1 were obtained. The objective of this project was to examine, analyze and characterize the surface deposits of the tube samples.

2.0 SAMPLE DESCRIPTION AND EXPERIMENTAL

2.1 Tube Sample Description

The inspection of the tube samples revealed the following features:

Tube R60S43

This sample tube arrived in three long (approximately 20 cm) and several shorter sections. The tube surface was covered with an extremely fine deposit of corrosion products. A schematic of the as-received tube is shown in Figure 1. The first break, "A", occurred at the top of the rolled region. A small piece between his break and a second break, "B", showed bands of a dull metallic color which were free of corrosion products. These bands were associated with corrosion damage. The section immediately above break "B" had a visible oxide/ deposit mark which corresponded to the top of the sludge pile. The distance

between the rolled joint and the mark was 90 mm. The measured sludge pile height in the region was 140 mm.

Immediately below the mark, there was another region with a band of the similar dull metallic color which was also indicative of tube damage. Microscopic examination of this areas showed the presence of small indentations with a bright copper colored deposit in the bottom. Some indentations had depths of up to 6um.

Tube R58S4

This tube arrived in three long sections. The tube was also covered on most of its surface with a fine film of corrosion deposits. A schematic of the as-received sections is shown in Figure 1. The bottom break of the tube had taken place in the bottom transition of the rolled joint. The tube section between this break and the top one corresponded to the tube region under the sludge pile. As in the previous tube, a brown colored oxide/deposit interface was noticeable at 95 to 110 mm from the top of the rolled joint. This interface corresponded to the top of the sludge pile.

Below the sludge pile interface and also immediately above the top of the rolled joint there was a region of bands of metallic color. This region was related to possible surface attack. The top section of this tube sample was covered with adherent and relatively thick surface deposits which upon microscopic examination showed to be porous. The deposits were thicker on the concave side of the curvature and it is likely that this is a result of the pulling procedure. The tube was pulled at an angle with respect to its axis and the deposits were scraped off the surface by the tubesheet orifice edge. The part of the tube near the top section and the intrados side of the curvature were minimally affected.

Tube R59S43

The tube arrived in two long sections and one smaller piece. One of the breaks had taken place at the top of the rolled joint. Between the two breaks there was a small tube piece, approximately 10 mm long. The remaining section showed a sludge pile bandat 80 to 100 mm above the top of the rolled joint. Above the band there were several patches of thick deposits.

Tube R46S36

The sample tube consisted of three long pieces. The bottom one included the complete rolled joint and the sludge pile interface

which was situated 10 to 20 mm from the top of the rolled joint. Immediately below the interface there was a band of metallic color similar to those on the other tube samples. Below the rolled joint there was indication of a leakage path extending 20 to 30 mm from the bottom joint transition.

Tube R69S51

There were a total of 20 pieces in this tube sample, 14 of which corresponded to the region below the rolled joint. The remaining six pieces were consecutive and had been at or above the rolled joint. The top and bottom transition of the rolled joint were in two separate pieces.

2.2 Sample Coupons for Analysis

The locations in the sample tubes of the specimens are depicted in Figure 1. Some tube sections were analyzed as received (specimens A and B). Coupons were cut from the tubes so that the specimens were amenable to spectroscopic examination.

2.3 Analytic Techniques

The tube samples were covered with an extremely thin coating of corrosion products. On most regions the tube surface was visible. Spectroscopic analytical techniques were ideal because of their surface sensitive nature and their non-destructive characteristics. Specimen coupons E and H were analyzed in their as-received form by ESCA (Electron Spectroscopy for Chemical Analysis). Subsequently the same coupons were analyzed by SIMS (Scanning Ion Mass Spectrometry) and finally by EDXA. Specimen coupons H and C were analyzed by SAM (Scanning Auger Spectroscopy). The remaining specimens were analyzed by EDXA .

3.0 **RESULTS**

3.1 EDX Analysis

Eighty nine analyses were performed. The detailed description of the areas analyzed and the results of the analyses are included in Appendix 7.1. The deposits were generally extremely thin. Some results had consequently strong contributions from the underlying metal.

There were some areas that showed copper-rich deposits near regions with attack. Figure 2 shows a copper-rich area in specimen A which had an adjacent region with surface attack. The copper-rich deposit had open areas through which the tube surface revealed.

Figure 3 shows specimen C which contained the rolled rolled joint region on the right side of the picture, the crevice region is situated immediately on the left. Further to the left there is a region with surface attack. The scattered deposits on the left side of the micrograph corresponded to the region under the sludge pile. Sulphur and chlorine concentrations were consistently high in these and any other deposits which had been originally under the sludge pile. In thick deposits on the tube surface but away from the sludge pile, sulphur had a similar concentration; however the chlorine concentration was lower.

Figure 4 shows an area with surface attack. The intergranular nature of the corrosion can be appreciated from the topography. The depth could not be estimated. The Ni/Cr ratio in the regions with damage and regions with practically no deposits were compared. The ratio for the damage areas was 4.2 (sd=1.00) based on 14 analyses covering an area several mm^2. The tube surface ratio was 3.4 (sd=0.8) based on 19 analyses. The difference was not statistically significant; however, there seemed to be some indication of chromium depletion on the damaged surfaces compared to the unattacked surfaces.

Figure 5 shows an area of specimen H in tube R58S42 which had a blob of darker deposits. Part of the deposits had spalled off the surface leaving a copper-coloured underlying deposit. The analysis of these deposits was particularly interesting. The analyses showed high sulphur concentrations approximately three to four times higher than in the deposits outside the blob; however, the chlorine concentration was the same. The high sulphur concentration in the blob scale was accompanied by high levels of silicon, magnesium and iron. The copper, zinc and aluminum concentrations were lower.

The underlying deposit inside the blob contained high concentrations of copper, nickel and chromium. These two elements originated from the underlying Inconel 600 material.

Compared to the deposit analysis of the sludge pile region of a tube from Bruce unit 3 steam generator 3, there seems to be a generally higher sulphur concentration in the deposits in these samples while silicon, calcium and magnesium concentrations are significantly lower here. The calcium concentration is particularly low.

3.2 ESCA Results

Two coupons were analyzed by ESCA. Specimen C contained a section of the rolled joint region, a damage region with surface

attack and a section with deposits which was situated under the sludge pile. Specimen H had thick deposits on all its surface and a circularly shaped blob with darker deposits which had partially spalled off showing an underlying deposit of copper-like appearance.

The description and results of the ESCA work are detailed in Appendix 7.2. Only the main conclusions are presented here. The surface analysis of specimen C showed the presence of silicon, magnesium and calcium in varying concentrations. The concentration of calcium was systematically lower than that of magnesium . The silicon and magnesium concentrations usually increased or decreased together.

Sulphur was detected in all the areas analyzed. No reduced sulphur species (sulphide) was detected. The sulphur peak generally showed a certain degree of complexity in most analyses; however, the species systematically identified was sulphate. In addition to this, on the thick deposit situated outside the blob in specimen H, a sulphur-oxygen species corresponding to a reduced inorganic sulphite was identified.

Chloride was consistently detected in all the surfaces analyzed. The deposit within the blob in specimen H contained significantly higher concentrations of iron than in the other deposits. The concentration of copper was higher in the underlying deposits within the blob. Copper was exclusively detected in its high oxidation state in the thick deposits in specimen H and in its lower oxidation state in the underlying deposit within the blob. The deposits under the sludge pile had a similar concentration of the two copper oxidation states.

3.3 SAM Results

Full details of the Auger analyses are given in Appendix 7.3. SAM spectra were obtained from the damaged region of specimen E (which also included a section of the rolled joint). Sulphur and chlorine were detected on the surface even after a 90 second sputtering . These elements seemed to be indigenous to the top layer.

Nitrogen was also detected; its concentration increased with the sputtering time. The chromium over nickel ratio decreased with sputtering time and the concentrations of chromium, nickel, and iron increased. Those for oxygen and carbon decreased with the sputtering time.

Specimen H (blob) was analyzed as well. The analysis of the underlying copper-like deposits confirmed high copper

concentrations. There was a thin layer containing carbon which quickly disappeared after 1 minute sputtering. The ratio between copper and oxygen, which was approximately one in the as-received surface, changed to seven after a five minute sputtering. At the end of that period, the copper concentration was greater than 80% of the detected elements.

Chlorine was measured before and after 1 minute of sputtering but was not detectable after five minutes. The thick deposit within the blob showed the presence of sulphur and chlorine and relatively high concentrations of oxygen, iron and copper. Zinc and potassium were also detected . Carbon was present at a level of 30%.

3.4 SIMS Results

Details of the SIMS results are given in Appendix 7.4. The complexity of the surfaces analyzed made the quantitative interpretation of the results very difficult. The bargraphs showed the presence of up to twenty elements most of which could be traced to the feedtrain materials. Lithium was an exception.

Elemental ion images suggested correlations between some species. For instance, the distributions for magnesium, aluminum, calcium and silicon coincided in most of the surfaces analyzed. A similar association existed between potassium, sodium and chloride. These correlations were not completely consistent and the complex topography of the sample could have contributed to the apparent elemental association.

4.0 DISCUSSION

All the areas that showed surface attack were situated in regions originally under the sludge pile. The deposits in these regions showed significant concentrations of contaminants such as chloride and sulphate. When compared to previous analyses of sludge pile deposits, the concentration of these two contaminants were significantly higher/1/. The higher concentrations of sulphur may be due to the acid excursion in January 1986.

The oxide layer in the area of attack contained sulphur and chlorine throughout its full depth and these compounds appear to be an integral part of the layer. There seemed to be some indication of chromium depletion on the area of damage but this conclusion is only tentative and in need of confirmation. The chromium depletion could be interpreted as a destruction of the protective layer. Passive films of Inconel 600, which formed under acidic sulphate conditions, tended to show chromium enrichment /2/. Also, areas of IGA attack showed chromium

depletion on the external oxide film /3/.

Some areas presented surface attack adjacent to copper-rich deposits. On the surface of these deposits there was some cuprous oxide with traces of cupric oxide. The oxide layer is thin and the underlying deposit is metallic copper. The copper-rich deposits are in close contact with the alloy 600 surface. Since cupric ion reduction is a cathodic reaction, the tube attack in the regions near the copper-rich deposits may have been enhanced by the copper reduction process. It is quite likely that there is surface attack under the deposits as well. This would be an indication that the electrochemical potential under the pile was quite aggressive.

The only region with copper deposits away from the sludge pile was in specimen H of tube R58S42. The presence of high concentrations of sulphate in the adjacent scale and its apparent porosity and thickness may be related to the copper reduction process.

The presence of sulphite in the deposits outside the blob is difficult to explain since sulphite is not thermodynamically stable at steam generator operating conditions; however, it may still form under certain conditions of pH, temperature and electrochemical potential. In fact, the reduction of sulphate by hydrazine to intermediate species such as elemental sulphur and sulphite is more favorable under acidic conditions. Alternatively, metallic copper may also reduce sulphuric acid to form sulphite and cupric ions at low pH/4/.

The conditions during and after the acid excursion may have been more favorable for sulphate reduction than those during normal operation; it is possible that the sulphite detected may have been a product of the abnormal chemistry.

The absence of more stable reduced sulphur species such as sulphide is however surprising and it casts some doubt on this hypothesis. Sulphide has been identified in the corrosion deposits of the Pickering steam generators. Another explanation for the presence of sulphite is that it may have been formed at low temperature immediately before or during the sampling operation.

Further analyses are necessary to ascertain or disprove the presence of reduced sulphur species in the steam generator since these compounds are know to induce IGA on alloy 600. Additional samples should be obtained from other units to find the extent of damage in each unit since different chemistries may have existed during and after the acid excursion.

If the damage observed was exclusively a consequence of the acid sulphate chemistry during the excursion, the rate of tube material attack is likely to have decreased after each shutdown since the aggressive environment would have leached out of the sludge pile. If, on the other hand, the attack is related to the presence of reduced sulphur species, which may have formed during the excursion, the rate of attack may still be significant. Future samplings may resolve this question.

Other deposits particularly under the sludge pile region and in thick scales contained important concentrations of silicon, magnesium, aluminum and calcium. The apparent association of these elements suggests the presence of a complex silicate or silicates among the corrosion products.

Similar conclusions have been reached in other steam generator deposit analyses. There is no evidence that associates the presence of these compounds with aggressive conditions in steam generator environments. On the contrary, silicates seemed to have some inhibiting effects on the IGA of alloy 600/5/.

5.0 CONCLUSIONS

1. The concentration of sulphur and chlorine were significantly higher in these tube deposits than in previous analyses. The high sulphur concentration may be due to the sulphuric acid excursion in January 1986.

2. Copper plated areas were adjacent to areas with surface attack. The rate of attack in the area may have enhanced by the copper ion reduction reaction. The attack appeared to be intergranular in nature.

3. Sulphite was identified in deposits away from the sludge pile. It may have been formed during the acid excursion but also during sampling. It is recommended that additional samples are obtained from this and other units to determine the present rate of the tube material attack, the extent of damage in other units and confirm the presence (or absence) of reduced sulphur species.

4. Complex silicates are present among the corrosion products. This presence may have some mitigating effect on the rate of tube attack.

ACKNOWLEDGMENTS

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S. Sandloehken for the SEM-EDX analyses
F. Greening and P. Ganza for SAM work
Prof. N.S. McIntyre (Surface Science Western) for ESCA work and interpretation.
Prof. N.S.McIntyre and G. Mount for SIMS work and interpretation.

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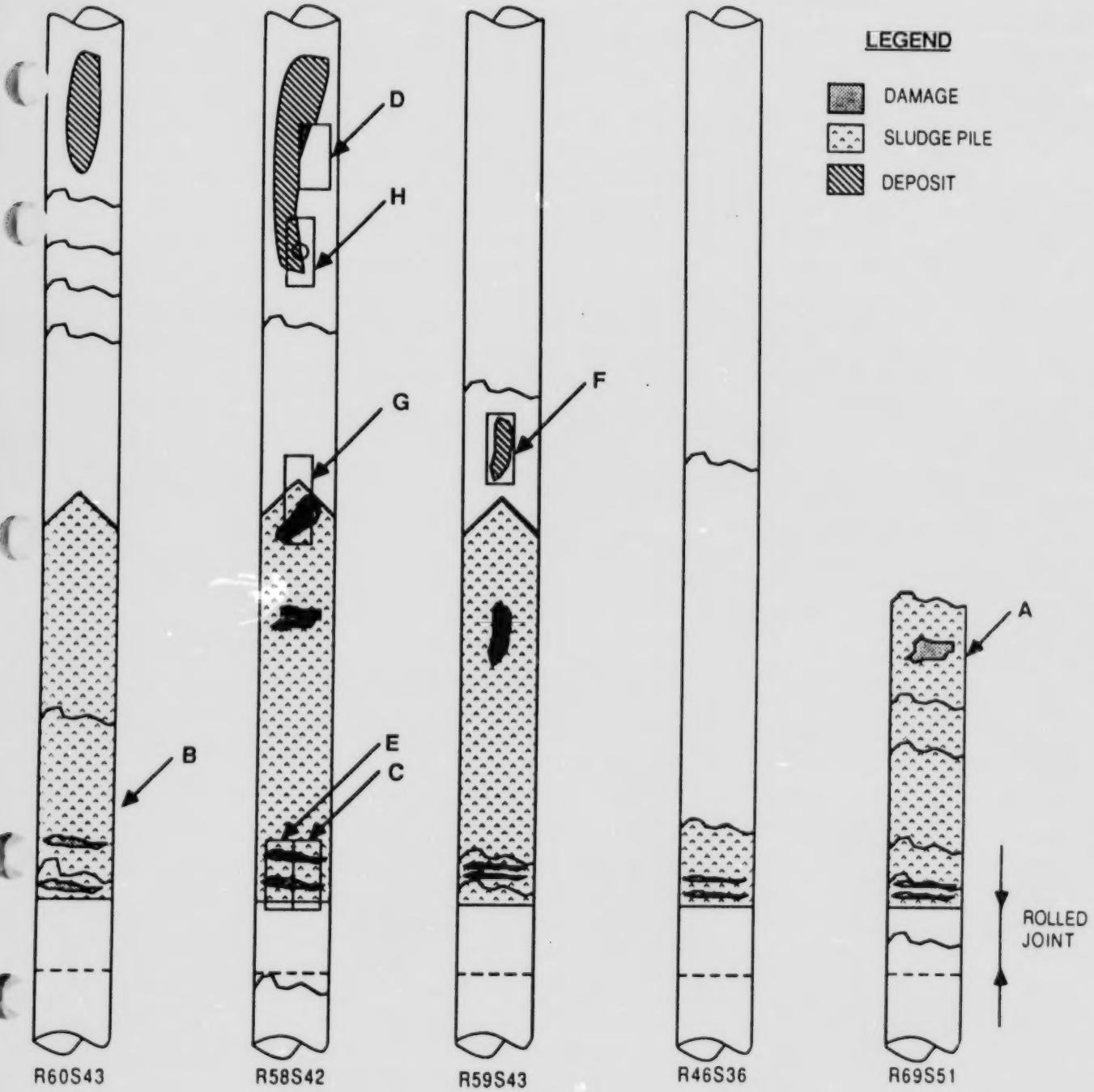


FIGURE 1

BRUCE NGS "A", UNIT 1, STEAM GENERATOR 3
TUBE SAMPLES AND ANALYSIS SPECIMEN LOCATION

DRAFTING-LB
PG1
175989 RD

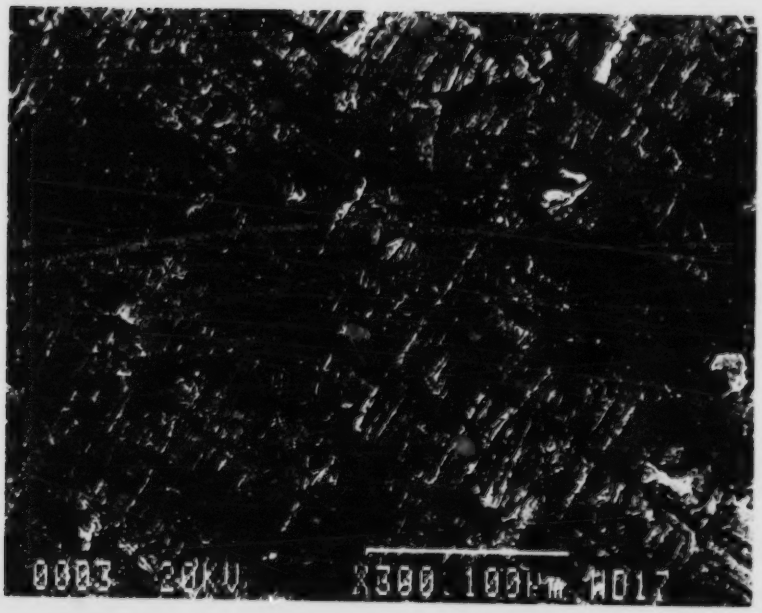


FIGURE 2

SPECIMEN A. (TUBE R69S51). COPPER-RICH AREA WITH AN ADJACENT REGION WITH SURFACE ATTACK

DRAFTING-LB
PG2
175985 RD

88-20

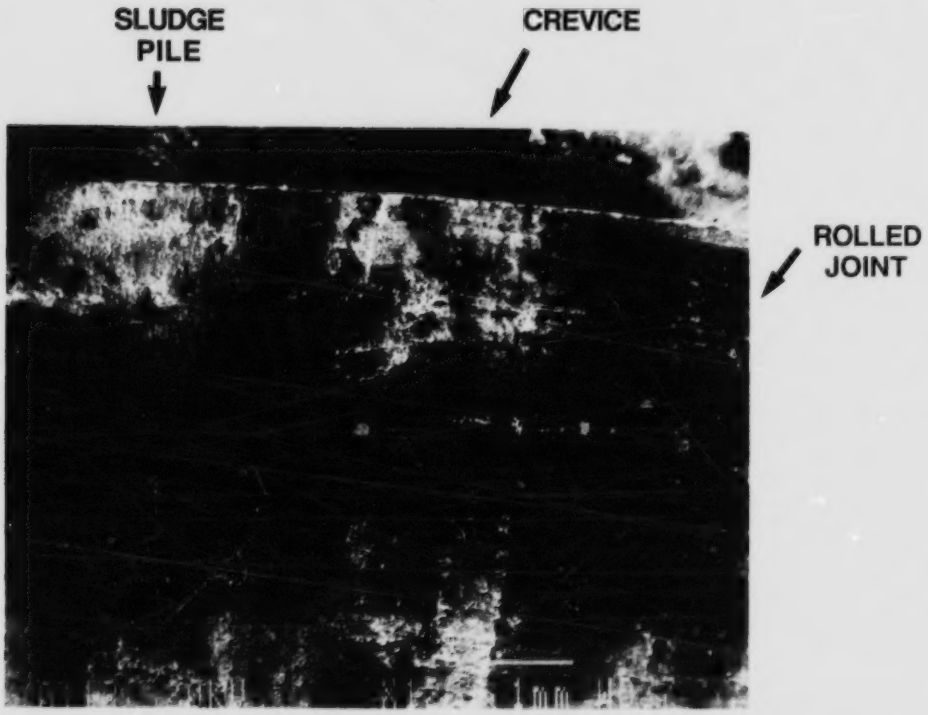


FIGURE 3

SPECIMEN C. (TUBE R58S42). VIEW OF THE ROLLED JOINT, CREVICE REGION AND SLUDGE PILE REGION. THE AREAS WITH SURFACE ATTACK ARE IN THE CREVICE REGION AND IMMEDIATELY ABOVE IT.

DRAFTING-LB
PG3
175986 RD

88-20

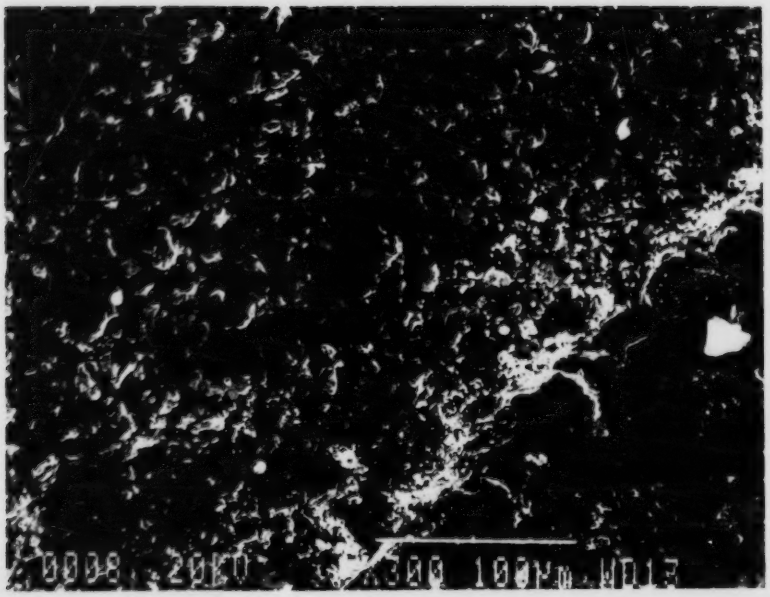


FIGURE 4

SPECIMEN C. (TUBE R58S42). AREA WITH SURFACE ATTACK

DRAFTING-LB
PG4
175987 RD

88-20

FIGURE 5

SPECIMEN H. (R58S42). THE MIGROGRAPH SHOWS THE BLOB OF CORROSION PRODUCTS. THERE IS A THICK SCALE WHICH COVERS PART OF THE SURFACE, THE REMAINDER HAS A THIN UNDERLYING COPPER-RICH DEPOSIT

DRAFTING-LB
PG5
175988

88-20

7.0 **APPENDICES**

7.1 EDXA Analyses

The EDX analyses were carried out in a Link AN10000 instrument capable of semiquantitative analysis. Table 7.1.1 presents the analysis description and the specimen analyzed. Table 7.2.2 shows the analytical data. Eighty nine analyses were carried out in total. The tube deposits were generally very thin and there was interference of the underlying tube alloy. The concentrations of nickel and chromium were typically high.

The highest silicon concentrations were found in the deposits above the tubesheet region. High silicon concentrations coincided with high magnesium and calcium although the calcium concentration was much lower than in previous analyses of Bruce steam generator tubesheet sludge pile deposits /1/.

Sulphur and chlorine concentrations were higher in these analyses than in the deposits from unit 3, steam generator 3.

TABLE 7.2.1

DESCRIPTION AND IDENTIFICATION OF EDXA RESULTS

TUBE	ANALYSIS	REGION DESCRIPTION	MGF
R69S51#6 (Spec.A)	1	Area scan on top of Cu deposit near region where it seems to be some attack	100
	2	Adjacent area also on top of Cu deposits but near the edge	100
	3	Area in region of attack with deposits	100
	4	Same area as before but including Ti,Zn,Al	100
	5	Localized deposits on surface	2000
	6	Same as before but including P	2000
	7	Analysis on a localized deposit on a different area	2000
	8	Analysis on a localized deposit on a different area	2000
	9	Same as before but including Mg	2000
	10	Analysis on a localized deposit on a different area	2000
	11	Area about 1.5 cm from the other end of the tube	100
	12	Analysis on a localized thick deposit	2000
	13	Analysis on an adjacent thick deposit	2000
	14	Area scan on the other end of the tube (likely under the sludge pile)	100
	15	Deposits on the area	2000
	16	Adjacent deposits on the same area	2000
R60S43 (Spec.B)	17	Area scan on area with possible damage (near the rolled joint)	300
	18	Tube surface without thick deposits	2000
	19	Same as before but detector at the correct distance.	2000
	20	Area with localized deposits	2000
	21	Area scan in the middle of sample, 2 cm from R.J. edge	100
	22	Adjacent area	100
	23	Adjacent area mostly free from deposits	2000
R58S42 (temp.) (Spec.C)	24	RJ region . Area showing attack	1000
	25	Area on rolled joint	1000
	26	Area on deposit next to region of attack	1000
	27	Area on adjacent deposit	1000
	28	Top of coupon under sludge pile	1000
	29	Area scan under sludge pile	100
	30	Area with attack	300
	31	Area with deposits in region of attack	300
	32	Area with attack	300

TABLE 7.2.1 (Cont.)

DESCRIPTION AND IDENTIFICATION OF EDXA RESULTS

TUBE	ANALYSIS	REGION DESCRIPTION	MGF
R58S42	33	Metal surface with light deposits	300
Thick De	34	Surface with thick deposits	300
(Spec.D)	35	Adjacent to previous analysis	300
	36	Round spot. Dark thick deposits	300
	37	Same. Adjacent area	300
	38	Same. Adjacent area	300
	39	Same. Adjacent area	300
	40	Area adjacent to thick deposits	2000
R58S42	41	Sludge region	300
R.J.	42	Adjacent sludge region	300
(Spec.E)	43	Sludge region General surface	30
	44	Area below damage. Crevice	300
	45	Area below damage	300
	46	Area below damage	300
	47	Base metal R.J.	300
	48	Area below damage	50
	49	Damage area	300
	50	Light phase in damage area	20000
	51	Dark phase in damage area	20000
	52	Dark phase in damage area	20000
	53	Light phase in damage area	20000
	54	Light phase in damage area	20000
	55	Dark phase in damage area	20000
	56	Dark phase in damage area	20000
R59S43	57	Thin deposits on coupon edge	300
Heavy De	58	Adjacent heavy deposits	300
(Spec.F)	59	Adjacent heavy deposits	30
	60	Open area. No heavy deposits	300
	61	End of coupon on heavy deposits	300
R58S42	62	Region with light deposits	300
SP/FTS	63	Adjacent region with thicker deposits	300
(Spec.G)	64	Few mm from edge	300
	65	Area with thick deposits	300
	66	Area with thin deposits	300
	67	Area near interface on white deposits	300
	68	Similar area (white deposits)	300
	69	White deposits	300
	70	Darker deposits	300
	71	Adjacent area with dark deposits	300
	72	Opposite end of coupon	300

TABLE 7.2.1 (Cont.)

DESCRIPTION AND IDENTIFICATION OF EDXA RESULTS

TUBE	ANALYSIS	REGION DESCRIPTION	MGF
R58S42	73	Deposit outside blob	100
BLOB	74	Deposit outside blob	100
(Spec.H)	75	Deposit inside blob	100
	76	Deposit inside blob	100
	77	Deposit inside blob	100
	78	Cu plated inside blob	100
	79	Cu plated inside blob	100
R58S42	80	Bright deposit in blob scale	2000
BLOB	81	Dark deposit in blob scale	2000
(Spec.H)	82	Deposit outside blob	60
	83	Deposit outside blob	60
	84	Deposit inside blob	60
	85	Deposit inside blob	60
	86	Light deposit within blob	2000
	87	Dark deposit within blob	2000
	88	Cu plated inside blob	60
	89	Cu plated inside blob	60

TABLE 7.1.2

EDXA RESULTS, DETECTED ELEMENT WEIGHT %

SAMPLE	ANALYS	MGF	Si	Mg	S	Cl	K	Ca	Cr	Fe	Ni	Cu	Al	Ti	Zn	P	Mn
R69S51	1	100	1.8	NA	0.9	1.0	0.1	0.2	6.9	6.0	30.3	52.9	0.0	0.0	0.0	0.0	0.0
As received.	2	100	1.1	NA	0.6	0.8	0.1	0.1	9.8	6.8	45.3	35.4	0.0	0.0	0.0	0.0	0.0
Piece showing	3	100	2.3	NA	0.9	1.1	0.1	0.3	14.5	14.2	60.2	6.4	0.0	0.0	0.0	0.0	0.0
Cu deposit	4	100	2.1	NA	0.8	1.0	0.1	0.2	13.6	13.2	55.5	6.0	2.9	0.2	4.4	0.0	0.0
At sludge lin	5	2000	6.5	NA	1.9	1.7	0.2	1.1	6.9	17.2	27.0	15.0	5.1	0.0	17.5	0.0	0.0
(Specimen A)	6	2000	6.6	NA	1.7	1.6	0.2	1.1	6.7	17.3	26.8	14.9	5.1	0.2	17.5	0.4	0.0
	7	2000	6.1	NA	2.5	2.3	0.0	1.8	1.1	24.7	6.4	20.2	14.6	0.2	18.2	2.0	0.0
	8	2000	5.5	NA	0.8	1.1	0.1	0.5	0.8	21.3	3.7	34.9	8.1	0.0	22.3	0.9	0.0
	9	2000	5.5	NA	0.8	1.1	0.1	0.5	0.7	20.7	3.9	34.1	7.7	0.1	22.7	0.8	1.5
	10	2000	3.4	NA	0.8	0.8	0.0	0.2	0.7	17.7	4.3	45.8	9.8	0.2	13.8	0.6	2.1
	11	100	2.9	NA	2.4	2.3	0.5	0.5	15.8	14.9	48.2	8.2	2.6	0.2	0.9	0.0	0.6
	12	2000	3.6	NA	4.8	4.1	0.4	0.8	5.9	19.8	35.3	21.1	1.3	0.1	1.7	0.0	0.9
	13	2000	1.6	NA	1.8	2.4	0.0	0.1	9.1	10.9	56.1	15.8	0.5	0.0	0.9	0.1	0.6
	14	100	3.3	NA	4.3	3.2	0.4	1.0	13.4	31.6	31.4	6.5	1.4	0.2	2.2	0.0	1.1
	15	2000	3.4	NA	6.0	4.1	0.5	1.7	8.9	44.3	20.3	5.6	4.6	0.0	2.0	0.3	1.1
	16	2000	1.6	NA	4.2	2.4	0.3	0.8	17.3	22.6	36.6	10.5	0.6	0.2	2.0	0.0	1.0
R60S43	17	300	0.6	NA	0.4	0.5	0.1	0.0	15.9	10.2	64.6	0.8	3.7	0.3	0.2	0.0	0.4
As received.	18	2000	0.5	NA	0.5	0.4	0.0	0.2	16.4	9.7	69.6	1.4	0.2	0.1	0.7	0.0	0.1
Piece above RJ	19	2000	0.5	NA	0.4	0.4	0.1	0.1	16.7	9.8	70.5	0.8	0.2	0.0	0.4	0.0	0.2
under SP	20	2000	1.5	NA	0.7	0.7	0.0	0.7	17.0	14.1	57.1	1.4	5.5	0.2	0.7	0.0	0.3
(Specimen B)	21	100	1.2	NA	1.1	0.8	0.2	0.2	24.5	14.4	48.7	6.5	0.6	0.2	1.5	0.0	0.2
	22	100	1.7	NA	1.3	0.8	0.1	0.4	21.5	15.0	50.9	5.8	0.6	0.2	1.6	0.0	0.3
	23	2000	1.2	NA	0.8	0.6	0.0	0.2	21.9	13.3	54.6	5.3	0.5	0.1	1.2	0.0	0.3
R58S42	24	2000	0.4	0.3	0.1	0.1	0.0	0.0	15.5	7.9	74.8	0.2	0.2	0.2	NA	0.0	0.1
RJ Attack eg.	25	2000	0.4	0.5	0.6	0.1	0.0	0.1	15.5	12.5	68.7	0.3	0.2	0.2	NA	0.0	0.8
(Specimen C)	26	2000	1.9	0.6	0.7	0.3	0.0	0.3	20.2	15.1	55.4	2.6	0.9	0.3	NA	0.1	1.6
	27	2000	3.0	1.2	3.3	1.7	0.1	0.1	23.6	23.6	36.6	2.4	0.8	0.3	NA	0.1	3.1
	28	2000	0.7	0.8	0.5	0.4	0.1	0.2	19.7	10.1	61.8	4.8	0.5	0.2	NA	0.0	0.3
	29	100	1.0	0.6	0.7	0.5	0.0	0.2	18.8	11.2	62.1	3.9	0.5	0.2	NA	0.1	0.3
	30	300	0.3	0.7	0.1	0.2	0.1	0.0	15.3	7.3	74.1	0.5	0.3	0.2	0.6	0.0	0.2
	31	300	3.3	1.3	1.8	0.3	0.1	0.4	26.1	19.4	23.1	13.4	1.0	0.2	5.6	0.0	3.9
	32	300	3.3	0.7	2.7	0.4	0.0	0.2	29.7	22.1	29.7	1.8	0.7	0.1	4.4	0.0	4.2
R58S42	33	300	0.7	0.6	0.2	0.1	0.1	0.2	14.3	13.3	61.0	3.6	1.2	0.1	4.2	0.1	0.4
Thick Deposit	34	300	4.5	2.4	0.6	0.1	0.2	0.6	0.1	27.9	3.2	38.8	3.5	0.1	16.1	0.2	1.7
(Specimen D)	35	300	4.3	2.2	0.8	0.2	0.2	0.5	0.2	28.6	3.3	38.1	3.6	0.0	15.5	0.5	1.8
	36	300	3.9	1.9	0.7	0.2	0.2	0.5	0.5	34.6	4.5	32.2	2.8	0.0	16.2	0.2	1.5
	37	300	3.1	1.8	0.5	0.2	0.2	0.4	0.4	32.3	4.4	36.5	3.1	0.0	15.4	0.3	1.4
	38	300	5.1	2.6	0.8	0.1	0.3	0.6	0.4	27.7	3.6	33.7	4.1	0.0	18.9	0.4	1.7
	39	300	3.8	2.2	0.6	0.1	0.2	0.4	3.2	26.3	15.2	29.6	3.1	0.0	13.7	0.2	1.6
	40	2000	1.2	0.7	0.2	0.1	0.1	0.1	13.1	17.3	54.2	3.5	2.0	0.3	6.4	0.1	0.7

TABLE 7.1.2 (Cont.)

EDXA RESULTS, DETECTED ELEMENT WEIGHT %

SAMPLE	ANALYS	MGF	Si	Mg	S	Cl	K	Ca	Cr	Fe	Ni	Cu	Al	Ti	Zn	P	Mn
R58S42	41	300	0.7	0.5	0.6	0.7	0.0	0.1	20.6	10.6	60.4	3.4	0.5	0.1	1.2	0.0	0.6
RJ Attack reg.	42	300	2.7	0.8	0.7	0.8	0.1	0.2	19.2	12.4	57.6	3.6	0.7	0.1	1.8	0.0	0.4
(Specimen E)	43	30	1.0	0.6	0.5	0.7	0.1	0.1	20.4	11.6	58.3	4.2	0.5	0.2	1.6	0.0	0.2
	44	300	1.6	0.6	0.9	0.9	0.1	0.2	20.3	12.3	56.7	3.2	0.8	0.2	1.7	0.1	0.4
	45	300	3.2	1.6	1.3	0.4	0.1	0.8	11.9	15.0	51.1	7.0	1.8	0.1	4.8	0.2	0.7
	46	300	1.6	1.2	0.9	0.3	0.0	0.4	14.0	14.0	61.3	2.3	1.1	0.2	2.3	0.0	0.5
	47	300	0.2	0.3	0.2	0.1	0.0	0.0	14.6	8.9	74.5	0.2	0.2	0.2	0.2	0.0	0.4
	48	50	2.6	1.4	1.4	0.6	0.2	0.5	14.5	16.3	54.1	3.5	1.2	0.3	2.6	0.1	0.8
	49	300	0.3	0.8	0.2	0.1	0.0	0.0	15.7	8.3	72.9	0.3	0.4	0.2	0.5	0.0	0.2
	50	20000	0.2	0.4	0.1	0.1	0.0	0.0	15.3	7.0	75.6	0.0	0.0	0.2	0.8	0.0	0.3
	51	20000	0.1	0.5	0.3	0.2	0.0	0.1	17.5	6.9	73.5	0.3	0.3	0.2	0.1	0.0	0.0
	52	20000	0.2	0.4	0.4	0.0	0.0	0.1	18.0	7.4	71.3	1.3	0.2	0.4	0.3	0.0	0.0
	53	20000	0.2	0.6	0.0	0.0	0.0	0.0	14.8	6.8	76.8	0.0	0.0	0.1	0.3	0.0	0.4
	54	20000	0.3	0.4	0.1	0.0	0.0	0.1	15.5	6.9	75.7	0.1	0.4	0.1	0.3	0.1	0.0
	55	20000	0.3	0.0	0.3	0.1	0.1	0.1	16.8	7.2	73.9	0.5	0.1	0.4	0.2	0.1	0.1
	56	20000	0.2	0.3	0.4	0.2	0.1	0.0	17.6	7.7	72.2	0.2	0.1	0.3	0.3	0.1	0.2
R59S43	57	300	7.9	2.9	1.3	0.4	0.4	1.1	1.0	36.0	5.1	19.4	3.7	0.0	18.2	0.3	2.4
Heavy Dep.	58	300	7.2	3.0	1.4	0.2	0.4	1.2	0.4	35.6	3.7	20.9	4.2	0.0	18.6	0.3	2.9
(Specimen F)	59	30	7.8	2.9	1.3	0.1	0.3	1.0	0.7	36.8	5.2	19.2	4.1	0.0	17.8	0.3	2.4
	60	300	1.9	0.9	0.3	0.1	0.2	0.2	12.9	19.1	45.8	6.9	2.2	0.2	8.3	0.1	1.0
	61	300	7.1	2.3	1.2	0.2	0.3	1.0	0.6	38.0	4.2	19.0	3.6	0.1	19.5	0.4	2.4
R58S42	62	300	2.7	1.1	1.8	1.6	0.1	0.6	17.8	15.0	47.1	7.6	1.0	0.2	2.6	0.1	0.7
SP/FTS	63	300	4.4	1.2	2.0	1.4	0.2	1.1	14.8	14.9	47.7	5.9	1.6	0.0	3.9	0.1	1.0
(Specimen G)	64	300	3.5	1.1	2.2	1.6	0.1	0.6	16.3	12.1	51.4	7.4	0.9	0.2	2.0	0.0	0.5
	65	300	3.3	1.0	1.8	1.0	0.2	0.8	16.5	13.1	54.2	3.4	1.0	0.2	2.8	0.2	0.6
	66	300	1.6	0.8	1.3	0.7	0.1	0.5	15.6	9.6	66.8	0.9	0.5	0.2	1.1	0.0	0.4
	67	300	0.7	0.4	0.4	0.2	0.1	0.2	15.4	7.8	73.2	0.4	0.3	0.2	0.4	0.0	0.2
	68	300	1.1	0.9	0.8	0.4	0.0	0.2	15.4	8.7	69.8	0.8	0.5	0.2	0.9	0.0	0.4
	69	300	7.8	1.1	1.5	0.9	0.1	0.5	17.0	14.0	47.9	3.7	0.7	0.1	3.8	0.0	1.0
	70	300	6.2	0.8	1.3	0.8	0.1	0.4	15.5	13.3	52.0	4.1	1.1	0.1	3.4	0.0	0.9
	71	300	3.5	1.4	0.8	0.6	0.1	0.1	12.5	13.0	57.7	3.1	2.0	0.2	4.0	0.0	1.2
	72	300	6.4	1.5	0.9	0.7	0.2	0.5	11.0	21.2	46.7	1.8	1.5	0.1	5.8	0.0	1.6

TABLE 7.1.2 (Cont.)

EDXA RESULTS, DETECTED ELEMENT WEIGHT %

SAMPLE	ANALYS	MGF	Si	Mg	S	Cl	K	Ca	Cr	Fe	Ni	Cu	Al	Ti	Zn	P	Mn
R58S42	73	100	5.1	2.7	1.0	0.2	0.4	0.7	1.4	27.1	6.9	32.9	3.8	0.1	15.3	0.3	2.3
BLOB	74	100	5.3	2.7	1.0	0.3	0.6	0.6	1.1	26.8	6.4	32.9	3.8	0.1	16.1	0.2	2.2
(Specimen H)	75	100	4.2	3.0	4.4	0.3	0.5	0.7	0.4	56.2	3.3	11.0	2.5	0.1	11.1	0.3	1.8
	76	100	4.0	2.3	3.3	0.3	0.9	0.3	0.7	57.0	3.9	12.7	2.3	0.0	10.3	0.4	1.5
	77	100	5.0	2.9	3.9	0.4	0.8	0.7	0.7	52.8	3.6	11.9	3.0	0.0	12.3	0.4	1.8
	78	100	1.0	1.8	0.3	0.2	0.1	0.1	3.4	10.8	12.6	65.1	1.0	0.1	3.3	0.1	0.3
	79	100	1.3	1.8	0.4	0.3	0.2	0.2	4.9	11.5	19.4	53.8	1.3	0.1	4.3	0.1	0.6
	80	2000	4.9	2.6	3.7	0.4	0.8	0.3	0.3	56.9	2.8	10.3	3.5	0.2	11.4	0.3	1.7
	81	2000	2.0	1.4	2.0	0.2	0.7	0.1	0.4	71.6	1.9	8.5	1.0	0.1	8.4	0.3	1.5
	82	60	5.0	2.8	1.1	0.3	0.4	0.7	0.5	28.1	4.3	33.9	3.5	NA	16.8	0.3	2.2
	83	60	4.5	2.4	1.0	0.3	0.4	0.6	0.4	29.8	3.8	33.5	3.1	NA	17.5	0.3	2.4
	84	60	3.2	1.6	3.1	0.7	0.6	0.2	0.4	66.0	2.3	10.2	2.0	NA	8.4	0.2	1.3
	85	60	3.2	1.7	2.5	0.4	0.6	0.5	0.3	50.6	2.7	19.9	2.0	NA	13.6	0.1	2.0
	86	2000	3.5	1.5	2.6	0.4	0.7	0.6	0.2	55.1	3.1	14.3	2.2	NA	13.7	0.2	1.9
	87	2000	4.1	1.6	3.9	0.9	0.7	0.2	0.6	64.7	2.5	8.1	2.4	NA	9.0	0.2	1.2
	88	60	1.4	2.1	0.4	0.4	0.1	0.1	5.3	11.6	19.7	52.2	1.5	NA	4.7	0.1	0.5
	89	60	1.3	1.3	0.4	0.3	0.1	0.2	6.2	13.7	24.4	44.4	1.4	NA	5.3	0.0	0.9

7.2 ESCA Analyses

Two specimens were analyzed by ESCA. Specimen C contained a small section of the rolled joint region, a damage area and a section covered with oxide and deposits which originally was under the sludge pile. Specimen H had a blob of dark colored scale underneath which there was a thin copper-rich deposit.

Two areas were arbitrarily selected in the sludge pile region of specimen C and analyzed. The results are shown in Figures 7.2.1 and 7.2.2. Carbon concentration is dominant (more than 80%) and this is due to sample contamination. The other elements detected included tin, magnesium and sulphur, from a S-O bond, in low concentrations of less than 1%. Silicon was present in the two analyses at about 5% concentration.

The damage region was also analyzed in duplicate, Figures 7.2.3 and 7.2.4, and the results showed high carbon contamination as well. Silicon was the only element detected in a significant concentration; tin sulphur iron and copper were found in concentrations less than 1%. The analysis of the rolled joint region, Figure 7.2.5, showed similar high carbon contamination and the presence of sodium silicon sulphur, chlorine, calcium and iron.

The sample was washed with trichloroethane and spectroscopic grade methanol to reduce the degree of carbon contamination. The binding energy of the carbon peak corresponded to that of a hydrocarbon C-C bond. Washing with organic solvents usually reduces the interference of the carbon peak. The cleaning was successful and a subsequent analysis of the rolled joint region, Figure 7.2.6, showed the carbon contribution reduced to 30% approximately .

In addition to the elements previously detected nickel and chromium were also quantified. Oxygen was the dominant peak in the spectrum thus indicating the presence of an oxide layer. The shape of the carbon peak indicated the possible presence of carbonate.

The damage area was re-analyzed, Figure 7.2.7, near the region where the analysis in Figure 7.2.4 had been taken. The spectrum showed high contributions of the oxygen and the carbon peaks with the possible presence of carbonate. Magnesium, chloride, sulphur and silicon were measured in significant concentrations. The energy of the sulphur was that corresponding to sulphate. Iron and zinc were also detected.

The analysis of the sludge pile region, Figure 7.2.8, showed the

presence of nitrogen with a binding energy corresponding to that of the N-H bond, however, only traces were detected. The concentrations of silicon and magnesium were significant and similar to those in the previous results.

Sulphur and chloride were in important concentrations. Again the binding energy for sulphur was that for sulphate. Feedtrain alloying elements such as iron, nickel, copper and zinc were also measured in relatively high amounts. Approximately 50% of the copper was present as Cu^{II} and the remainder as Cu^{I}.

Several analyses were carried out in the different areas of specimen H. The analysis of the thick deposits within the blob, Figure 7.2.9, showed a dominant concentration of carbon contaminant and oxygen. Silicon and magnesium had similar contributions when compared to previous analyses as well as chloride and sulphur.

There were two binding energies related to sulphur. One corresponding to sulphate and the other to another sulphur-oxygen species such as an inorganic sulphite. However the resolution of the spectrum was not sufficiently high to confirm this finding.

Feedtrain elements such as zinc, copper and iron were also measured. The contribution of iron was higher than in previous analyses. Practically all the copper was determined to be Cu^{II}. In a subsequent analysis of another adjacent area within the blob, Figure 7.2.9A, the elemental concentrations and identity of the main constituents was confirmed. In this analysis, the copper contribution was also mainly from Cu^{II} with only traces of Cu^{I}.

The presence of sulphate and a possible other sulphur-oxygen compound was confirmed although the sulphate contribution to the total sulphur peak was significantly greater.

The analysis of the underlying deposit within the blob, Figure 7.2.10, indicated a high concentration of copper which was detected mainly as Cu^{I} with approximately 25% Cu^{II}. The shape of the sulphur peak in the spectrum also showed the possible presence of a second sulphur-oxygen species in addition to sulphate. The number of scans was insufficient to sort out definitely the nature of the second contributor.

Magnesium, silicon and chloride were also detected and found to be in similar concentrations as in the previous analyses. Iron and zinc were also quantified in the analysis as significant contributors. A second analysis in an adjacent area, Figure 7.2.10A, confirmed these conclusions with copper mainly present

in its lower oxidation state.

The heavy deposits outside the blob, Figure 7.2.11, had high concentrations of silicon, magnesium and calcium. Chloride was also detected but in lower concentration. Aluminum was also significant as well as the feedtrain metals: iron, zinc and copper. Most copper was detected as Cu^{II} (75 % approximately) and the remainder was Cu^{I}. The shape of the sulphur peak indicated the possible presence of a second sulphur-oxygen species.

A second series of ESCA analyses was carried out on specimen H to address specifically the question of the oxidation state of the sulphur detected . The three significant regions, the underlying deposit within the blob, the heavy deposit within the blob and the deposit outside the blob were analyzed. The quantitative results correspond to Figures 7.2.12, 7.2.13 , and 7.2.14 , respectively.

Detailed spectra of the sulphur binding energies showed the absence of reduced sulphur species such as sulphide in the surface deposits. The only sulphur species detected within the blob was sulphate. No other species either in the heavy deposit or in the copper-rich underdeposit could be confirmed. The complexity of the sulphur peak was due to differential charging and not to a sulphur-oxygen species different from sulphate. The presence of inorganic sulphite was confirmed in the deposits outside the blob.

DH4_01A

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.7	0.0	-.3	0.000	1	9005	0	
Sn3d	486.6	0.0	1.6	22.048	1	2337	114	.25
Mg a	305.2	0.0	-.8	4.046	1	481	128	.28
C 1s	284.7	0.0	.1	1.000	1	35560	38199	82.37
S 2p 5°	163.3	0.0	-.7	1.793	1	82	49	.11
S 2p 5-0	169.7	0.0	5.7	1.793	1	245	147	.32
Si2p	102.1	0.0	2.1	.903	1	2091	2487	5.36
Zn3p	88.1	0.0	1.1	3.146	1	190	65	.14
Cu3p	78.4	0.0	4.4	2.774	1	544	211	.45
Fe3p	56.9	0.0	.9	1.885	1	398	227	.49
O2S	25.8	0.0	0.0	.161	1	712	4749	10.24
								100.0%

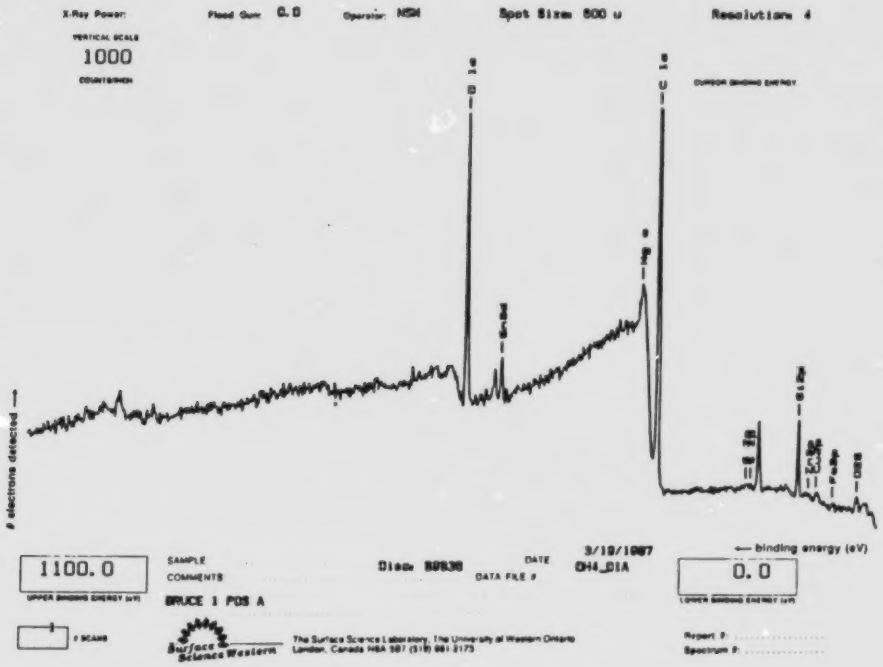


FIGURE 7.2.1

SPECIMEN C (ROLLED JOINT) "AS RECEIVED"
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF DEPOSIT UNDER THE SLUDGE PILE

SURFACE COMPOSITION TABLE

OH4_01B

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	532.8	0.0	.8	2.494	2	0	0	0.00
Sn3d	487.7	0.0	2.7	22.048	2	3564	87	.16
Mg a	306.2	0.0	-.8	4.046	2	1016	135	.25
C 1s	284.7	0.0	.1	1.000	2	86571	45498	96.82
Mo3d	231.0	0.0	4.0	9.816	2	670	37	.07
S 2p	168.7	0.0	4.7	1.793	2	244	73	.14
Cu3p	78.4	0.0	4.4	2.774	2	269	52	.10
O2S	26.9	0.0	0.0	.161	2	1172	3911	7.30
Si2s	153.6	0.0	4.6	1.029	2	5294	2763	5.16
								100.0%

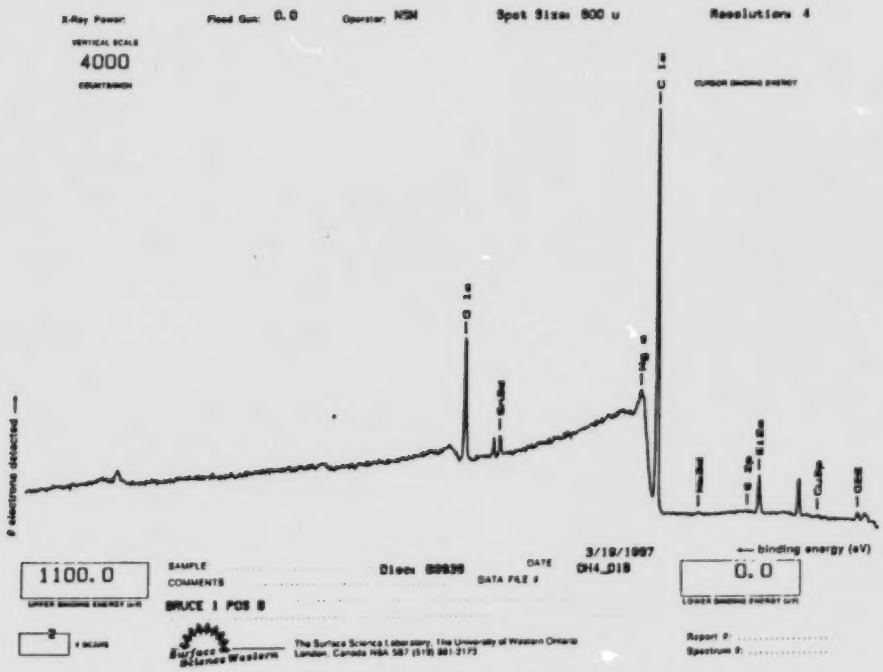


FIGURE 7.2.2

SPECIMEN C (ROLLED JOINT) "AS RECEIVED"
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF DEPOSIT UNDER THE SLUDGE PILE

SURFACE COMPOSITION TABLE

DH4_01C

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	532.8	0.0	.8	2.494	1	7541	3249	5.76
Sn3d	488.8	0.0	3.8	22.048	1	616	30	.05
C 1s	284.7	0.0	.1	1.000	1	46776	50248	89.07
Si2p	102.1	0.0	2.1	.903	1	2427	2887	5.12

								100.0%

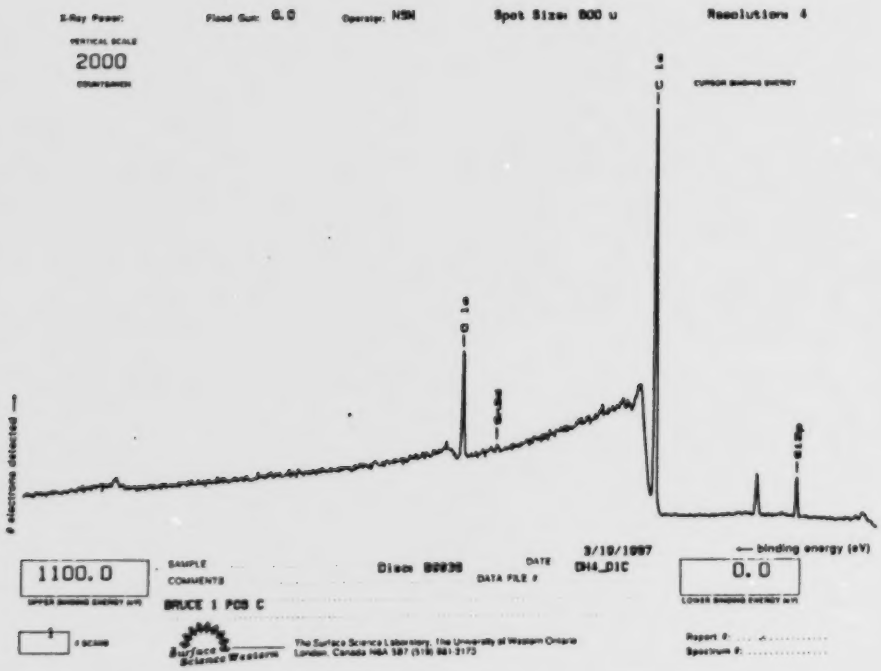


FIGURE 7.2.3

SPECIMEN C, (ROLLED JOINT) "AS RECEIVED"
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF AREA SHOWING SURFACE ATTACK

SURFACE COMPOSITION TABLE

OH4_01D

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	532.8	0.0	.8	2.494	2	13299	2864	6.22
C 1s	285.7	0.0	1.1	1.000	2	74771	40160	87.26
S 2p	169.7	0.0	5.7	1.793	2	328	98	.21
Cu3p	78.4	0.0	4.4	2.774	2	561	109	.24
Fe3p	56.9	0.0	.9	1.885	2	228	65	.14
O2S	26.9	0.0	0.0	0.000	2	429	0	
S12p	103.1	0.0	3.1	.903	2	4583	2726	5.92
								100.0%

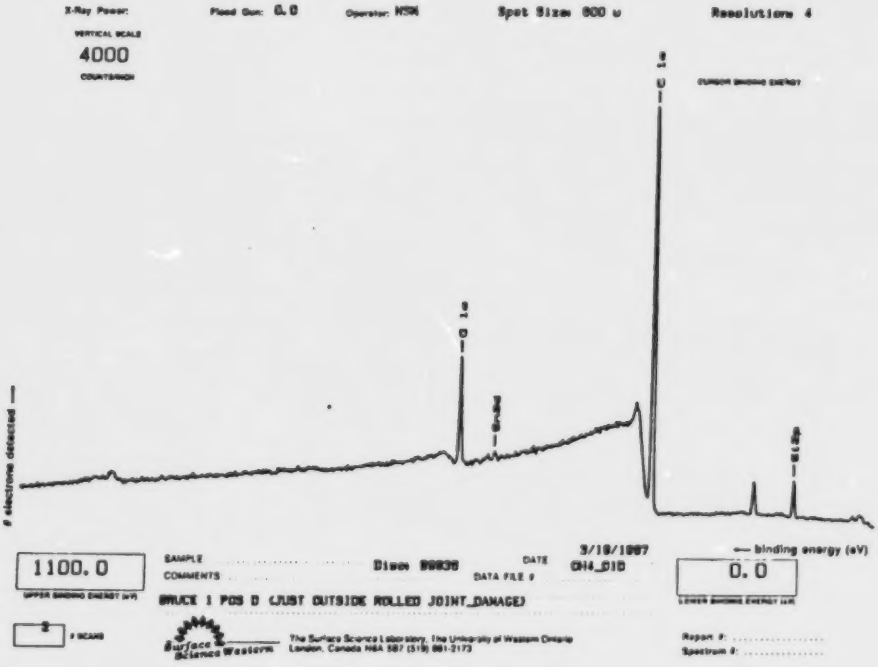


FIGURE 7.2.4

SPECIMEN C, (ROLLED JOINT) "AS RECEIVED"
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF AREA SHOWING SURFACE ATTACK

SURFACE COMPOSITION TABLE

OH4_01F

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.7	0.0	-.3	2.494	1	4776	2057	16.32
Na_a	499.5	0.0	2.5	2.967	1	438	159	1.26
Ca2p	352.3	0.0	4.3	4.881	1	267	59	.47
C 1s	284.7	0.0	.1	1.000	1	9080	9754	77.35
Cl2p	199.8	0.0	-1.2	2.335	1	338	152	1.20
S 2p	167.6	0.0	3.6	1.793	1	160	96	.76
Si2p	102.1	0.0	2.1	.903	1	185	220	1.75
Fe3p	56.9	0.0	.9	1.885	1	200	114	.90
								100.0%

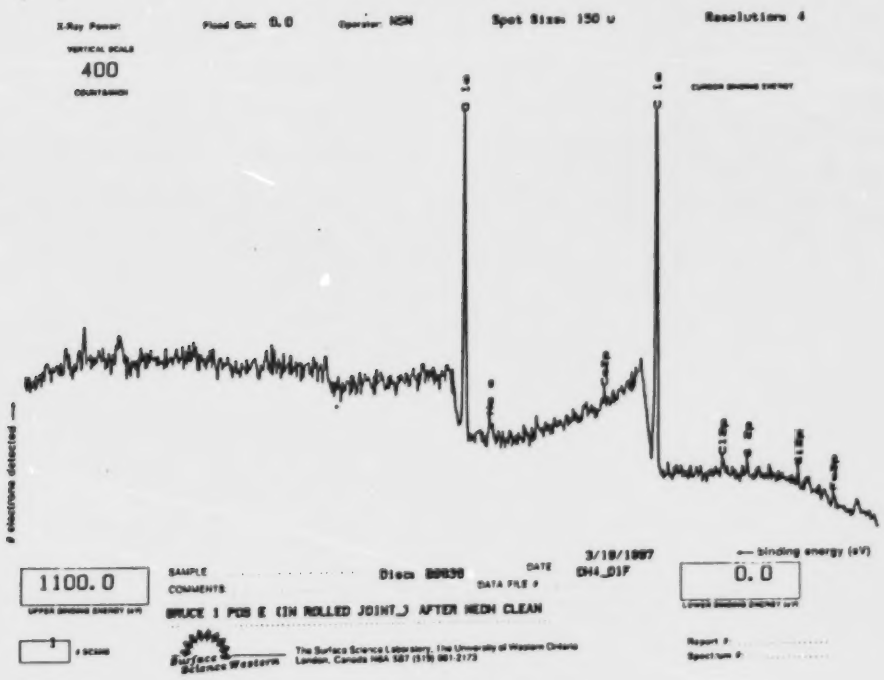


FIGURE 7.2.5

SPECIMEN C, (ROLLED JOINT) AFTER METHANOL CLEANING
ESCA SPECTRUM AND CALCULATED SURFACE
COMPOSITION OF ROLLED JOINT AREA

SURFACE COMPOSITION TABLE

OH4_011

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	528.3	1.0	-3.7	2.494	5	196947	15270	44.44
N 1s	396.5	1.0	-2.5	1.678	5	1544	180	.52
Ca2p	348.7	1.0	.7	4.891	5	5611	265	.77
Mg a	302.8	1.0	-4.2	4.046	5	14209	686	2.00
C 1s	282.3	1.0	-2.4	1.000	5	62716	12249	35.65
Cl2p	197.3	1.0	-3.7	2.395	5	7032	573	1.67
S 2p	166.0	1.0	2.0	1.793	5	4429	482	1.40
P 2s	188.5	1.0	-.5	1.245	5	550	86	.25
Si2p	99.6	1.0	-.4	.903	5	8133	1759	5.12
Zn3p	86.0	1.0	-1.0	3.146	5	8671	538	1.57
Cu3p	74.2	1.0	.2	2.774	5	12982	907	2.64
Ni3p	68.4	1.0	.4	2.490	5	4284	336	.98
Fe3p	53.7	1.0	-2.3	1.885	5	9910	1027	2.99
								100.0%

100.04

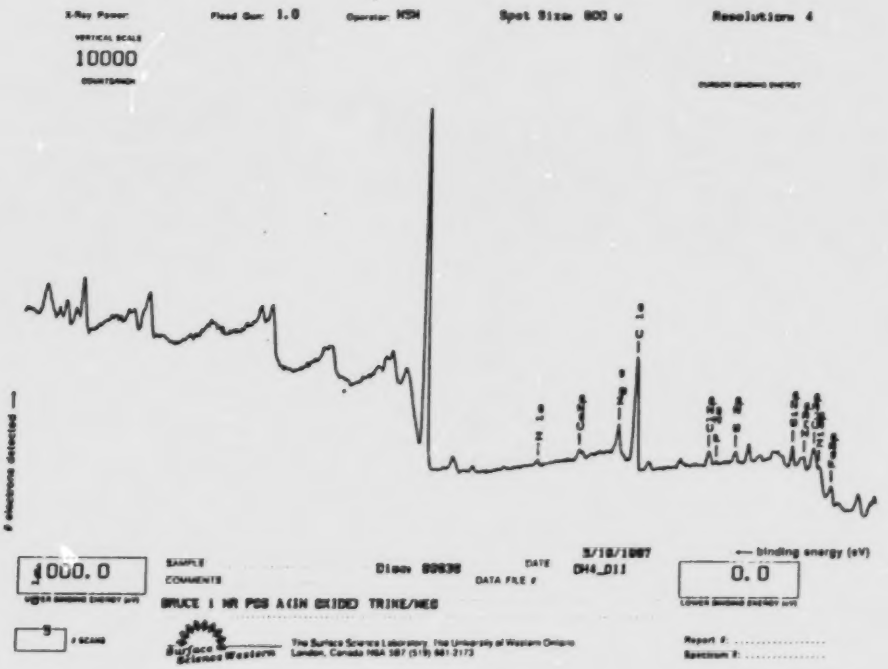


FIGURE 7.2.6

SPECIMEN C, (ROLLED JOINT) AFTER CLEANING
UNDERLYING ESCA SPECTRUM AND CALCULATED SURFACE
COMPOSITION OF ROLLED JOINT REGION

SURFACE COMPOSITION TABLE

OH4_01H

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	536.1	0.0	4.1	2.434	2	80402	15744	44.58
N 1s	405.3	0.0	6.3	1.679	2	27	8	.02
Ca2p	353.5	0.0	5.5	4.881	2	2030	203	.57
Mg a	310.5	0.0	3.5	0.046	2	4647	561	1.59
C 1s	289.1	0.0	4.5	1.000	2	29260	14287	40.46
Cl2p	203.1	0.0	2.1	2.395	2	4130	854	2.42
S 2p	173.8	0.0	9.8	1.793	2	2564	698	1.98
Si2s	158.2	0.0	9.2	1.029	2	3129	1484	4.20
Zn3p	93.8	0.0	6.8	3.146	2	4266	662	1.97
Fe3p	60.5	0.0	4.5	1.885	2	3143	814	2.30

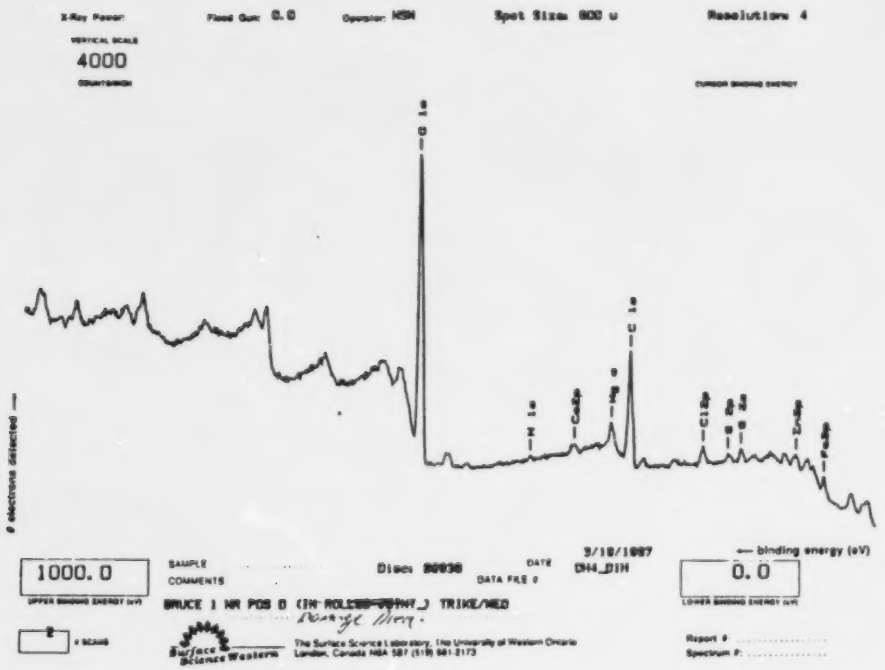


FIGURE 7.2.7

SPECIMEN C, (ROLLED JOINT) AFTER CLEANING
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF AREA SHOWING SURFACE ATTACK

SURFACE COMPOSITION TABLE

OH4_01G

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.7	0.0	-.3	2.494	8	44062	2373	52.13
Na a	499.5	0.0	2.5	2.367	8	3206	145	3.19
Ca2p	350.2	0.0	2.2	4.801	8	1158	32	.70
Mg a	308.3	0.0	1.3	4.046	8	2921	97	2.13
C 1s	285.7	0.0	1.1	1.000	8	11213	1506	33.08
Cl2s	268.6	0.0	-1.4	1.704	8	1208	95	2.09
S 2p	168.7	0.0	4.7	1.793	8	495	37	.81
Si2p	103.1	0.0	3.1	.903	8	376	56	1.23
Ni3p	67.7	0.0	-.3	2.490	8	1302	75	1.66
Fe3p	56.9	0.0	.9	1.885	8	1498	107	2.34
Cr3p	44.0	0.0	1.0	1.333	8	288	29	.64

100.0%

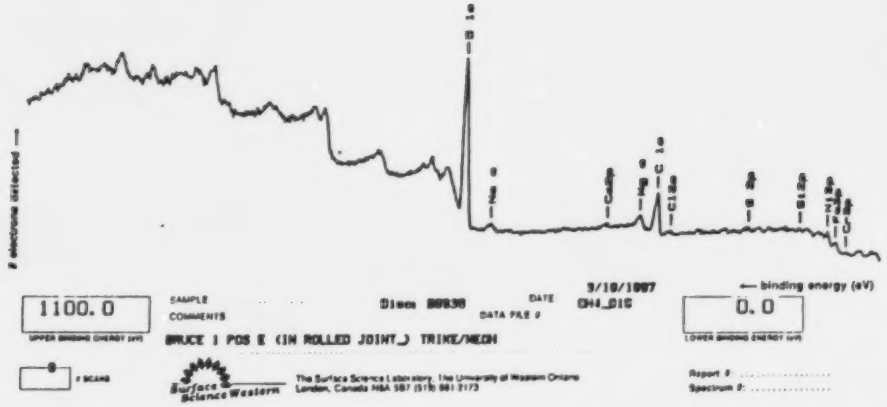
100.0%

File OH4_01G from Thursday 3/19/1987
BRUCE 1 POS E (IN ROLLED JOINT_) TRIKE/MEOH

NSM

X-Ray Power: Flood Gun: 0.0 Operator: NSM Spot Size: 150 u Resolution: 4

VERTICAL SCALE
4000
COUNTS/SEC



1100.0
UPPER BINDING ENERGY (eV)

SAMPLE
COMMENTS
Dion 88830
DATE 3/19/1987
DATA FILE # OH4_01G

← binding energy (eV)

0.0
LOWER BINDING ENERGY (eV)

BRUCE 1 POS E (IN ROLLED JOINT_) TRIKE/MEOH

SCANS

Surface Science Western
The Surface Science Laboratory, The University of Western Ontario
London, Canada N6A 5B7 (519) 661-2173

Report #:
Spectrum #:

FIGURE 7.2.8

SPECIMEN C (ROLLED JOINT) AFTER CLEANING
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF DEPOSIT UNDER THE SLUDGE PILE

Iteration [illegible] Chi-square [illegible]

SURFACE COMPOSITION TABLE

OH4_02A

Elem	Corrected B.E	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.3	1.0	-.7	2.494	3	104717	13671	42.30
Mg a	306.7	1.0	-.3	4.046	3	7628	614	1.93
C 1s	285.2	1.0	.6	1.000	3	34983	11388	35.73
Cl2p	198.3	1.0	-2.7	2.395	3	2390	305	1.02
S 2p 3/2	166.4	1.0	2.4	1.793	3	1141	207	.65
S 2p 1/2	169.2	1.0	5.2	1.793	3	3093	561	1.76
Si2s	154.3	1.0	5.3	1.029	3	2092	662	2.08
Zn3p	91.2	1.0	4.2	3.146	3	1755	182	.57
Cu3p	77.2	1.0	3.2	2.774	3	7408	969	2.73
Fe3p	56.7	1.0	.7	1.885	3	19643	3388	10.64
								100.00

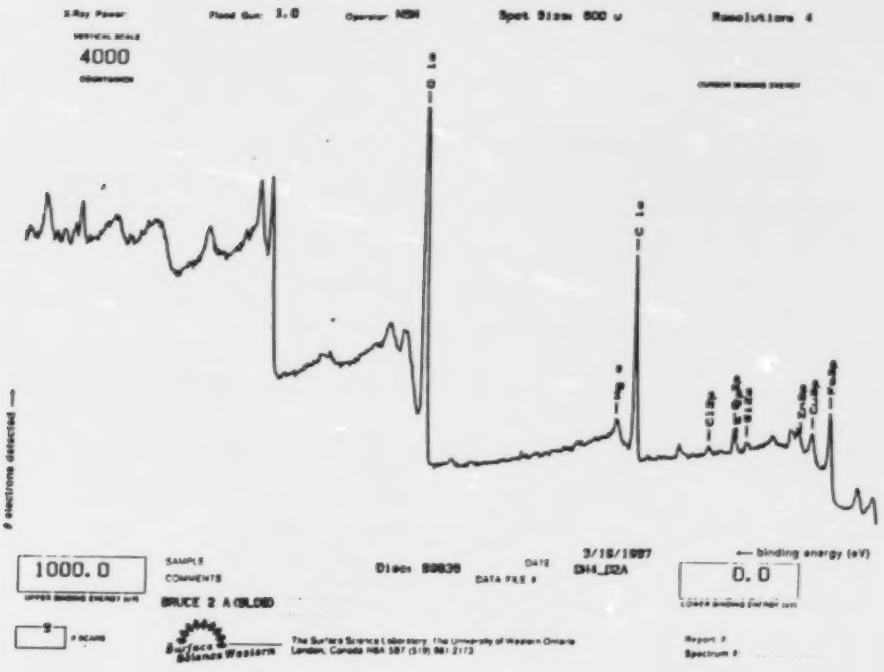


FIGURE 7.2.9

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF THICK DEPOSIT WITHIN THE BLOB

SURFACE COMPOSITION TABLE

OH4_020

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	534.2	1.0	2.2	2.494	5	0	0	0.00
N 1s	402.4	1.0	3.4	1.678	5	1350	157	.45
Ca2p	354.5	1.0	6.5	4.881	5	1833	73	.21
Mg a	309.6	1.0	2.6	4.046	5	13416	648	1.87
C 1s	288.1	1.0	3.5	1.000	5	52628	10279	29.74
Cl2p	202.2	1.0	1.2	2.395	5	2338	191	.55
S 2p	172.9	1.0	8.9	1.793	5	7064	769	2.23
Si2s	157.3	1.0	8.3	1.029	5	2659	505	1.46
Cu3p	80.1	1.0	6.1	2.774	5	15957	1123	3.25
Fe3p	55.6	1.0	3.6	1.885	5	37257	3860	11.17
O2S	26.4	1.0	0.0	.161	5	13708	16621	48.08
Zn3p	93.6	1.0	6.6	3.146	5	5506	342	.99
								100.02

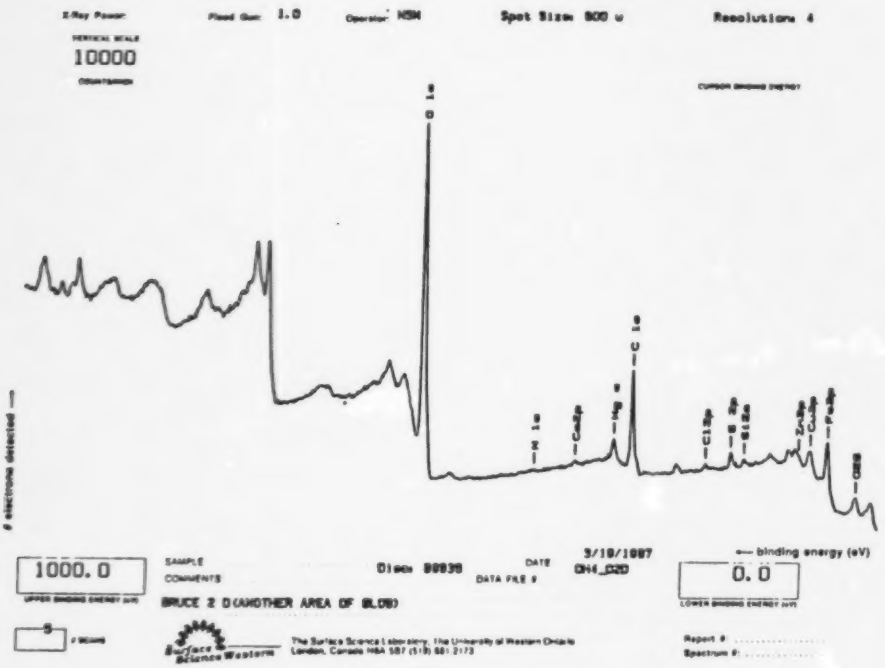


FIGURE 7.2.9A

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF THICK DEPOSIT WITHIN THE BLOB

SURFACE COMPOSITION TABLE

OH4_02R

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.3	1.0	-.7	2.494	3	0	0	0.00
Ca2p	350.6	1.0	2.6	4.881	3	2300	193	.64
N 1s	399.4	1.0	.4	1.678	3	737	143	.47
Mg a	304.7	1.0	-2.3	4.046	3	9604	773	2.54
C 1s	285.2	1.0	.6	1.000	3	23181	7545	24.81
Cl2s	269.6	1.0	-.4	1.704	3	1835	351	1.15
S 2p	168.0	1.0	4.0	1.793	3	3780	686	2.26
Si2s	152.4	1.0	3.4	1.029	3	3294	1042	3.43
Cu3p	76.2	1.0	2.2	2.774	3	49424	5739	19.07
Fe3p	55.7	1.0	-.3	1.885	3	2052	354	1.16
ZN3S	139.7	1.0	0.0	1.127	3	1376	397	1.31
O2S	23.5	1.0	0.0	.161	3	6507	13130	43.17
								100.0%

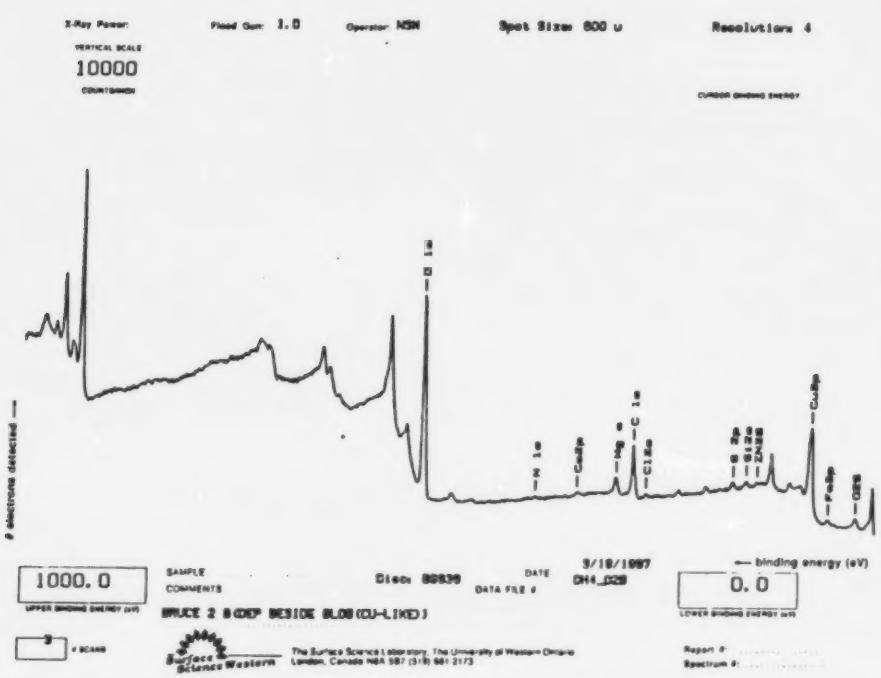


FIGURE 7.2.10

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF UNDERLYING DEPOSIT WITHIN THE BLOB

SURFACE COMPOSITION TABLE

OH4_02E

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.3	1.0	-.7	2.494	2	0	0	0.00
Ca2p	349.6	1.0	1.6	4.881	2	3470	347	.85
Mg a	304.7	1.0	-2.3	4.046	2	12019	1450	3.53
C 1s	285.2	1.0	.6	1.000	2	22069	10776	26.25
Cl2p	199.2	1.0	-1.8	2.395	2	3023	616	1.50
S 2p	165.5	1.0	1.5	1.793	2	1411	394	.94
Si2s	153.3	1.0	5.0	1.793	2	2014	549	1.34
ZN3S	137.7	1.0	4.3	1.029	2	7673	1743	4.24
Cu3p	76.2	1.0	0.0	1.128	2	669	298	.71
Fe3p	55.7	1.0	2.2	2.774	2	37692	6633	16.16
O2S	23.5	1.0	-.3	1.885	2	1273	330	.80
			0.0	.161	2	5925	17935	43.69
								100.02

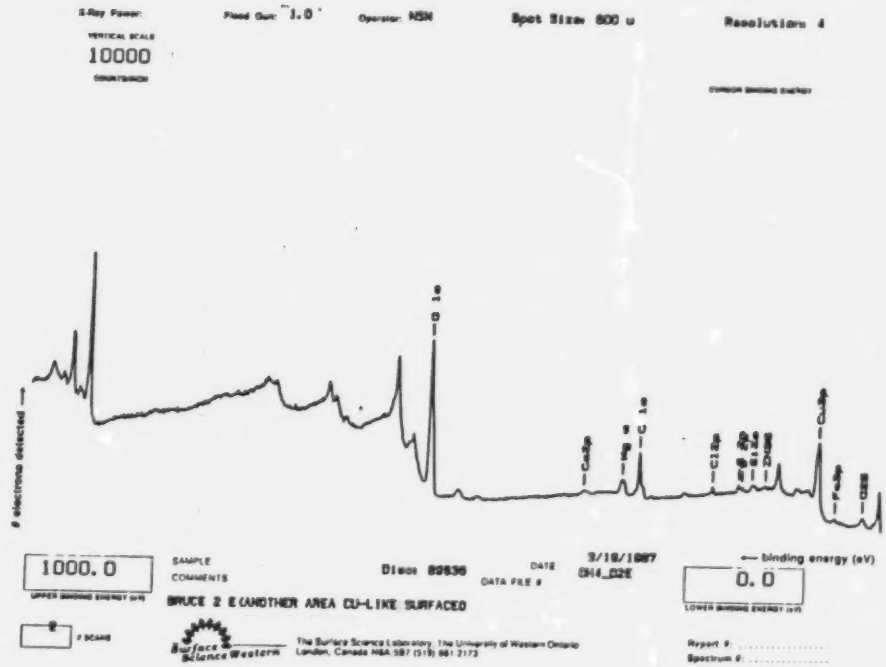


FIGURE 7.2.10A

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF UNDERLYING DEPOSIT WITHIN THE BLOB

SURFACE COMPOSITION TABLE

OH4_02C

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	528.3	1.0	-3.7	2.494	5	184662	14464	43.51
Ca2p	348.7	1.0	.7	4.881	5	11430	457	1.38
Mg 2	303.7	1.0	-3.3	4.046	5	35235	1701	5.12
C 1s	282.3	1.0	-2.4	1.000	5	50243	9813	29.52
Cl2p	196.3	1.0	-4.7	2.395	5	2415	137	.59
S 2p	166.0	1.0	2.0	1.793	5	5343	582	1.75
Si2s	150.4	1.0	1.4	1.029	5	11094	2105	6.33
ZN3S	137.7	1.0	0.0	1.128	5	4042	700	2.11
Fe3p	53.7	1.0	-2.3	1.885	5	8214	851	2.56
Al2s	117.3	1.0	-.7	.825	5	5251	1244	3.74
CU3S	120.9	1.0	0.0	1.047	5	6050	1129	3.40
								100.0%

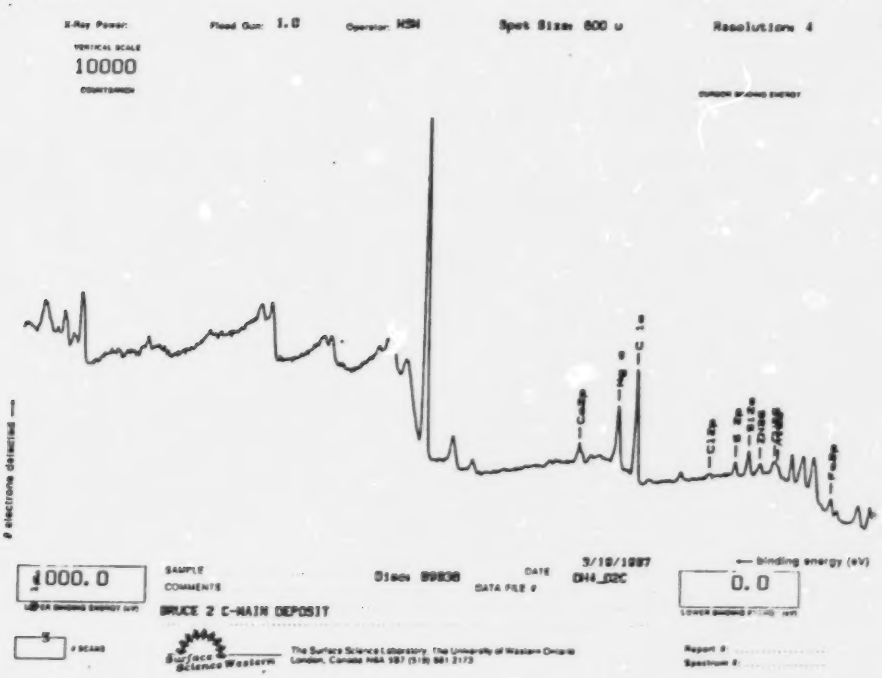


FIGURE 7.2.11

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF DEPOSITS OUTSIDE THE BLOB

RS8542 'Cu-PLATED' REGION SURVEY

Loaded into spectral area 2

SURFACE COMPOSITION TABLE

OH_2403_4

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	531.3	0.0	-.8	2.494	1	0	0	0.00
Ca2p	351.6	0.0	3.6	4.881	1	691	138	.69
Mg a	306.6	0.0	-.4	4.046	1	2572	621	3.11
C 1s	284.2	0.0	-.4	1.000	1	5243	5120	25.62
Cl2p	199.2	0.0	-1.8	.395	1	487	199	.99
S 2p	168.0	0.0	4.0	1.793	1	711	387	1.94
S 2p	161.1	0.0	-2.9	1.793	1	145	79	.40
Si2p	103.5	0.0	3.5	.903	1	1247	1349	6.75
Cu3p	75.2	0.0	1.2	2.774	1	8555	3011	15.07
Fe3p	56.6	0.0	.6	1.885	1	381	197	.99
ZN3S	140.6	0.0	0.0	1.126	1	613	532	2.66
O2S	24.4	0.0	0.0	.161	1	1378	8350	41.79
								100.0%

X-Ray Power: Flood Gun: 0.0 Operator: RNS Spot Size: 1000 u Resolution: 4

VERTICAL SCALE

2000

COUNTS/SWEEP

CURSOR BINDING ENERGY

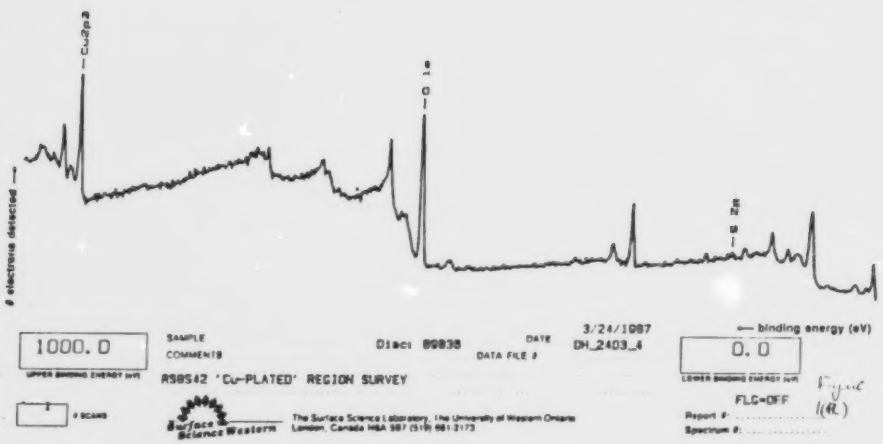


FIGURE 7.2.12

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING. ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION OF UNDERLYING DEPOSITS WITHIN THE BLOB

OH_2403_1

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	529.3	1.0	-2.7	2.494	1	0	0	0.00
Mg a	304.7	1.0	-2.3	4.046	1	1890	456	3.27
C 1s	283.2	1.0	-1.4	1.000	1	8963	8753	62.83
Cl2p	196.3	1.0	-4.7	2.395	1	842	343	2.46
S 2p	167.0	1.0	3.0	1.793	1	1087	592	4.25
S 2p	161.2	1.0	-2.8	1.793	1	64	35	.25
Si2s	152.4	1.0	3.4	1.029	1	737	699	5.02
Zn3p	92.8	1.0	5.8	3.146	1	684	212	1.53
Cu3p	75.2	1.0	1.2	2.774	1	2055	723	5.19
Fe3p	54.7	1.0	-1.3	1.885	1	4031	2119	15.21
O2S	22.5	1.0	0.0	0.000	1	2171	0	
								100.0%

X-Ray Power: Flood Gun: 1.0 Operator: RNS Spot Size: 1000 u Resolution: 4

VERTICAL SCALE
2000
COUNTS/INCH

CURSOR BINDING ENERGY

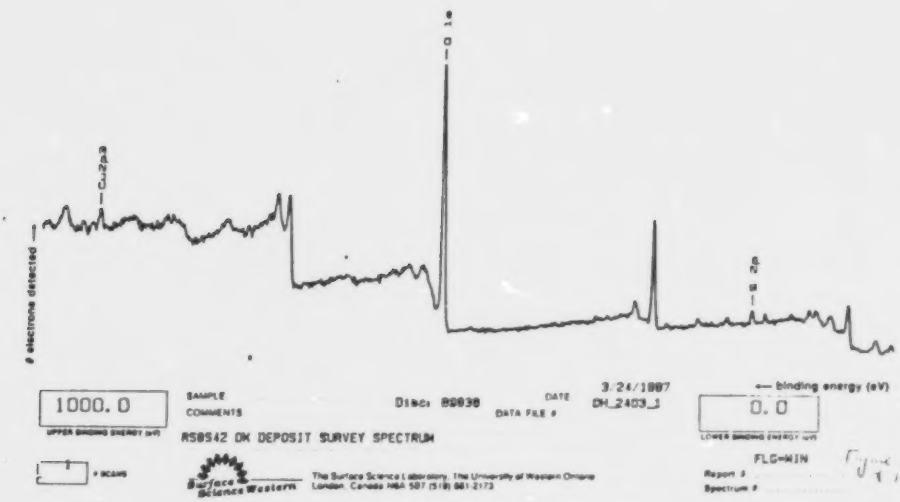


FIGURE 7.2.13

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF THICK DEPOSITS WITHIN THE BLOB

File OH_2403_1 from Tuesday 3/24/1987
RS8S42 DK DEPOSIT SURVEY SPECTRUM

Loaded into spectral area 3 RNS

SURFACE COMPOSITION TABLE

OH_2403_11

Elem	Corrected B.E.	Flood Gun EV	Delta B.E.	Sens Factor	# of Scans	Area	Relative Area	Atom %
O 1s	528.3	1.0	-3.7	2.490	1	27962	10951	29.51
Ca2p	347.7	1.0	-.1	4.881	1	1427	285	.77
Mg a	302.8	1.0	-4.2	4.046	1	5679	1370	3.69
C 1s	281.3	1.0	-3.3	1.000	1	7671	7491	20.19
Cl2p	195.3	1.0	-5.7	2.795	1	1270	518	1.39
S 2p	166.0	1.0	2.0	1.793	1	596	324	.87
Si2s	150.4	1.0	-4.8	1.793	1	41	22	.06
Zn3p	86.8	1.0	1.4	1.029	1	2036	1931	5.21
Cu3p	74.2	1.0	-1.0	3.146	1	3630	1127	3.04
Ni3p	65.5	1.0	.2	2.774	1	4559	1605	4.32
Fe3p	53.7	1.0	-2.5	2.490	1	311	122	.33
O2S	21.5	1.0	-2.3	1.885	1	1183	616	1.66
			0.0	.161	1	1776	10742	28.95
								100.0%

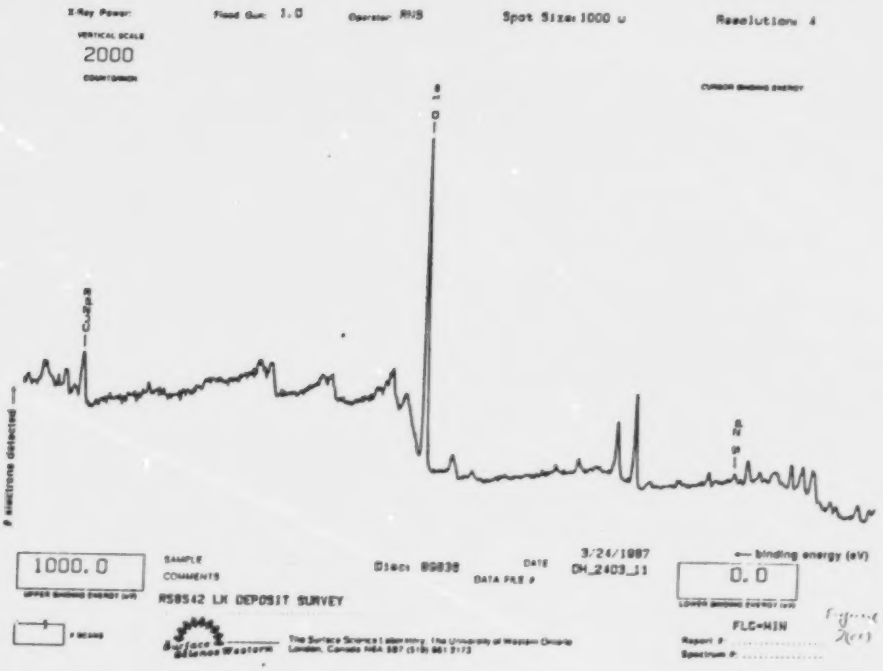


FIGURE 7.2.14

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
ESCA SPECTRUM AND CALCULATED SURFACE COMPOSITION
OF DEPOSITS OUTSIDE THE BLOB

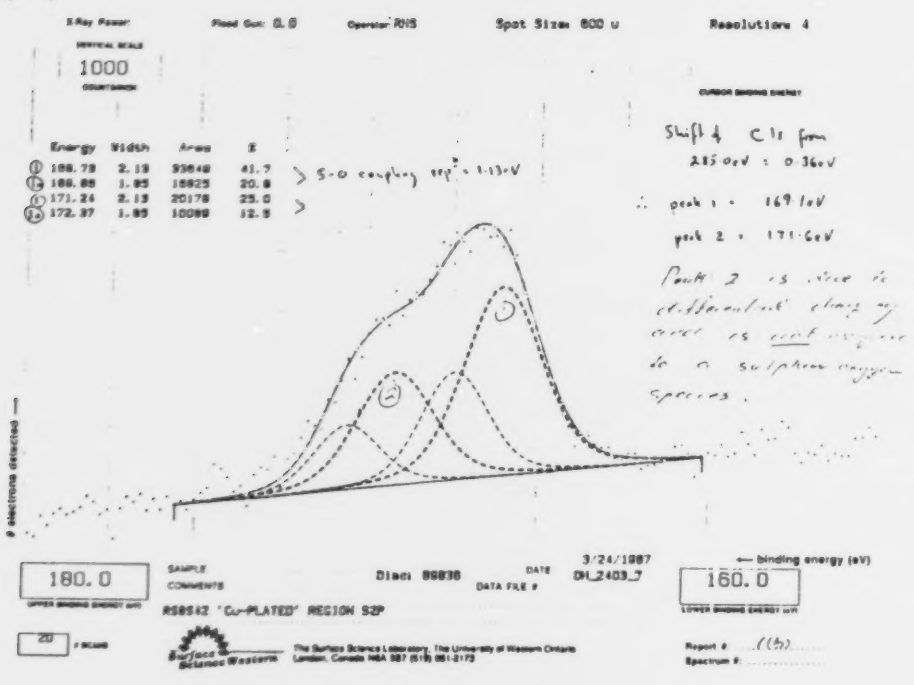


FIGURE 7.2.15

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
DETAILED ESCA SPECTRUM OF THE SULPHUR B.E.
ON THE UNDERLYING DEPOSITS WITHIN THE BLOB

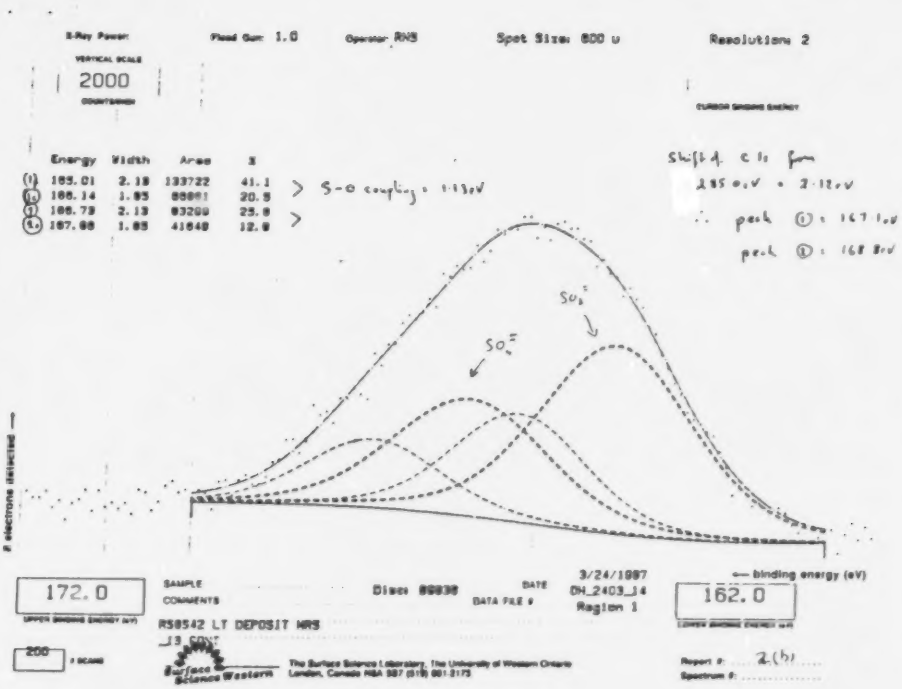


FIGURE 7.2.16

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
DETAILED ESCA SPECTRUM OF THE SULPHUR B.E.
ON THE DEPOSITS OUTSIDE THE BLOB

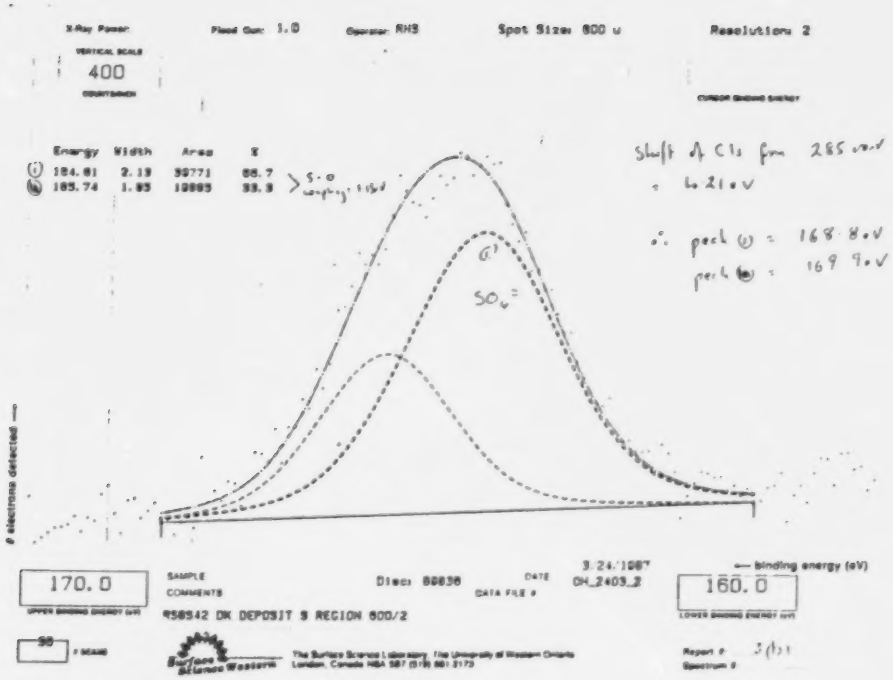


FIGURE 7.2.17

SPECIMEN H (HEAVY DEPOSITS AND BLOB) AFTER CLEANING.
DETAILED ESCA SPECTRUM OF THE SULPHUR B.E.
ON THE THICK DEPOSITS WITHIN THE BLOB

7.3 SAM Analysis

Specimens E and H were analyzed by SAM. The analyses of the damage region in specimen E are shown in table 7.3.1.

TABLE 7.3.1

SPECIMEN E. SAM ANALYSIS OF DAMAGE REGION.
ATOM %. BEAM DE-FOCUSSED TO 50 um DIAMETER

Analysis	Element									Comment
	S	Cl	Cr	Ni	Fe	Cu	O	N	C	
1	1.5	1.1	2.4	3.4	2.3	1.0	23	1.6	64	As received
2	3.6	2.6	2.2	4.6	3.6	1.4	25	1.5	56	30 s sputt.
3	1.5	1.2	4.6	11	6.4	1.7	41	2.3	30	30 s sputt.
4	1.8	1.0	3.3	16	6.3	-	34	2.9	35	90 s sputt.
5	1.3	1.3	8.8	29	7.4	-	27	3.6	22	90 s sputt.

In its as-received condition, the damage region seemed to be covered with a deposit layer with a high carbon content. The carbon concentration decreased after sputtering for a few seconds. The contribution of the base metal constituents, iron, nickel, and iron followed an opposite trend. The concentrations increased with sputtering time.

The as-received surface was analyzed (analysis 1). Two spots were selected after sputtering within the area sputtered. Analyses were taken at 30 seconds and 90 seconds analyses 2 and 4; and 3 and 5 , respectively. Sulphur and chloride showed essentially the same concentration throughout the sputtering period. The persistence of chlorine with sputtering time confirmed that it was an integral part of the oxide layer.

The oxygen contribution decreased with time (analyses 3 and 5); this suggested than the oxide layer in the region was quite thin since significant changes occurred after only 90 seconds of sputtering; however, the decrease could also be produced because of preferential sputtering of the oxygen atoms. In another spot (analyses 2 and 4), the oxygen concentration appeared to increase; however, it was generally found that the oxygen concentration was inversely related to that of carbon. The concentration of carbon in analyses 2 was much higher than in analysis 4 and that could explain the apparent oxygen increase. The presence of nitrogen is interesting, its concentration increased with sputtering time. Copper was present only in the

top layer, it was undetectable after a short sputtering time.

The analyses on specimen H are included in table 7.3.2. The underlying layer of deposits had a high concentration of copper which increased to 82 % after a sputtering period of five minutes. The as-received top layer showed similar concentrations of copper and oxygen as well as a important

TABLE 7.3.2

SPECIMEN H. AUGER ANALYSIS OF
SURFACE DEPOSITS ON BLOB REGION. % ATOM.
BEAM DE-FOCUSED TO A DIAMETER OF 50 um

Ana.	Element									Commemt
	S	Cl	Ni	Fe	Cu	Zn	O	K	C	
1	-	1.7	1.7	8.0	22	-	25	-	42	Under. As rec.
2	-	1.4	-	5.0	24	-	21	-	50	Under. As rec.
3	7.0	-	-	-	50	-	43	-	-	Under. As rec.
4	-	1.9	5	-	74	-	20	-	-	Under. 1 min.
5	-	-	6	-	82	-	12	-	-	Under. 5 min.
6	2.1	0.9	3.0	24	6.0	-	33	-	31	Scale. As rec.
7	2.0	0.7	-	14	14	6.7	29	2.3	31	Scale. As rec.

concentration of carbon which disappeared after 1 minute of sputtering. The oxygen concentration decreased with sputtering time. Chlorine, iron and sulphur were present in the top layer but became non-detectable after five minutes of sputtering. The contribution on nickel became more important after sputtering.

The scale within the blob had detectable amounts of sulphur and chlorine and important concentrations of iron, copper , oxygen, zinc and carbon. No sputtering was carried out on the surface.

7.4 SIMS Analyses

The SIMS equipment used was a Cameca IMS 3F in microscope. It uses a primary ion beam (in this case oxygen rastered over the sample to sputter material off the surface. Some of this sputtered material is itself ionized and can be accelerated and mass separated.

By maintaining the same ion spatial arrangement throughout the spectrometer, ion images can be obtained. Ion images can show the species that occur together on the same sample surface. Secondary ions can be directed into an electron multiplier for ion quantification. However, quantitative results are difficult without standards because of differences in the ion yields, matrix effects and molecular interferences.

Specimens C and H were analyzed by SIMS. Bargraphs for the damage, the rolled joint, and the sludge pile regions of specimen C are shown in Figures 7.4.1 to 7.4.3. The absence of a reliable element of reference makes the quantitative comparison of the analyses very difficult. All the surfaces analyzed show the presence of up to twenty elements, all of them justifiable in the feedtrain balance of plant materials.

In addition to the elements already identified by EDX antimony, sodium, lithium, and hydrogen were detected. The quantitative contribution of each element to the surface composition could not be determined since the ion yields may vary several orders of magnitude depending on the element.

Figures 7.4.4 to 7.4.6 show analyses on different regions of specimen H. The same elements in different proportions were identified. Because of the complexity of the analyses it was not possible to obtain quantitative information. Figure 7.4.7 shows the ion yields for a number elements. For example there is a difference of a factor of a thousand between magnesium and chloride.

Ion images were obtained for the areas of interest in the two specimens investigated. The topography of the surfaces made the interpretation of the images very difficult and no clear elemental correlations could be established. In most areas there seemed to be some correlation between magnesium, aluminum, silicon and calcium (Figure 7.4.8). In some other regions sodium, potassium and chloride appeared together. Sulphur was distributed quite evenly in most of the surfaces analyzed. Chromium and titanium on the other hand were generally present in discrete domains. Iron was also evenly spread throughout the surfaces analyzed.

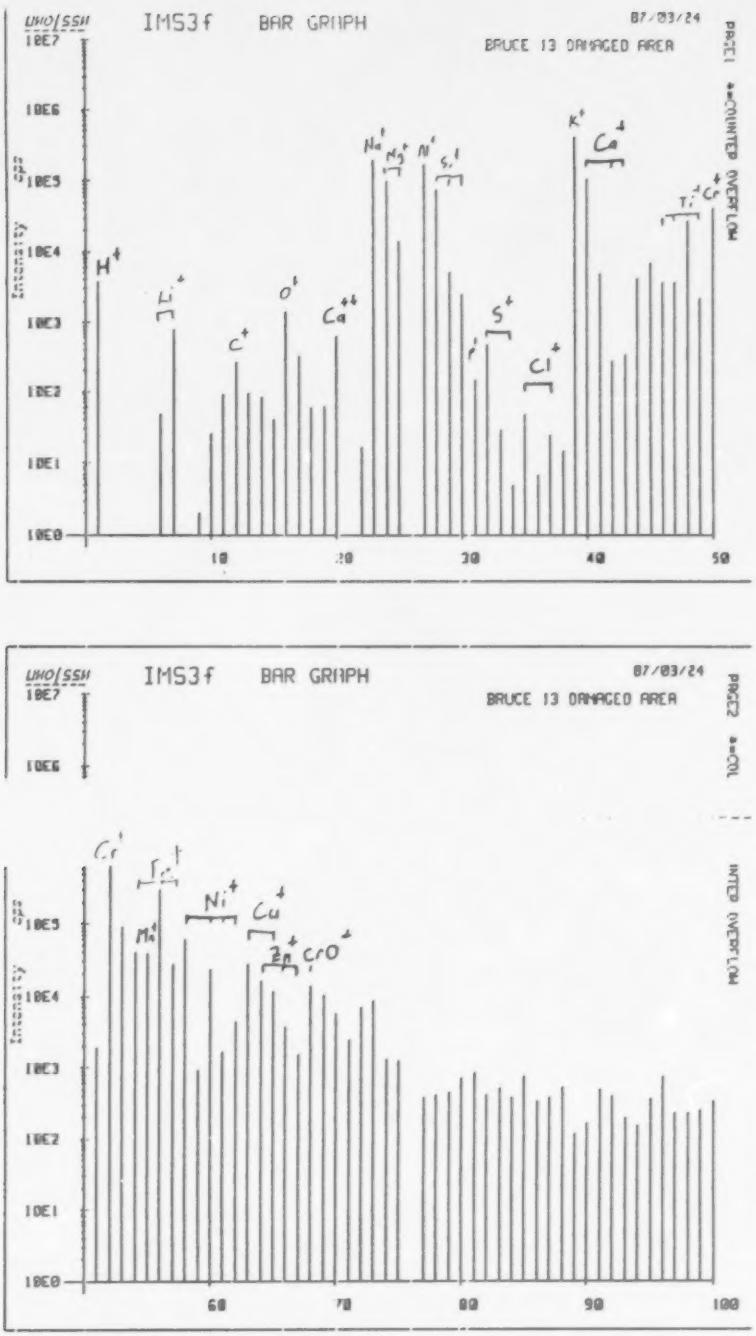
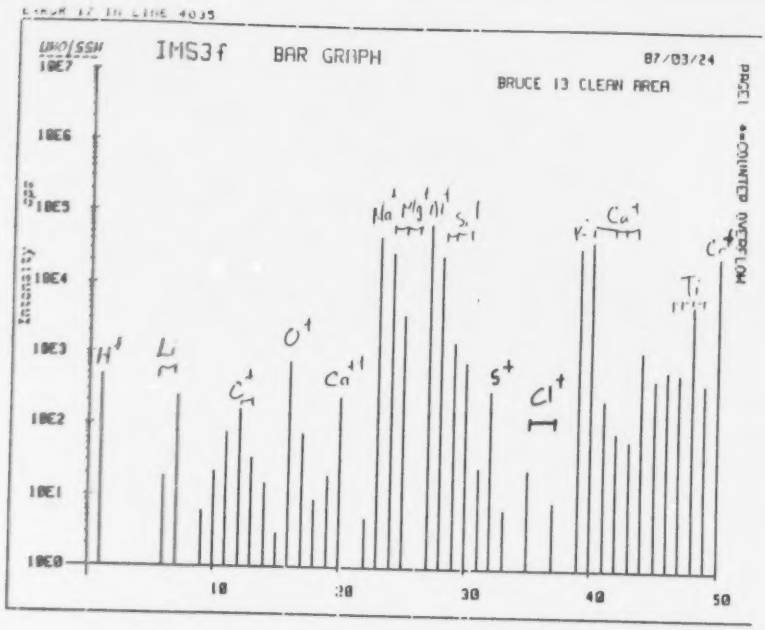


FIGURE 7.4.1

SPECIMEN C. SIMS ANALYSIS OF DAMAGE REGION



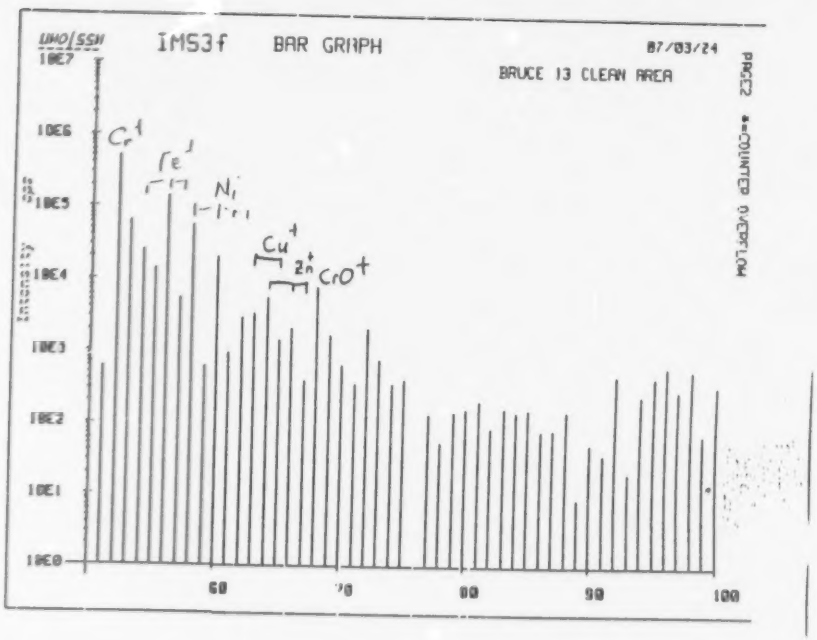


FIGURE 7.4.2

SPECIMEN C. SIMS ANALYSIS OF
ROLLED JOINT REGION

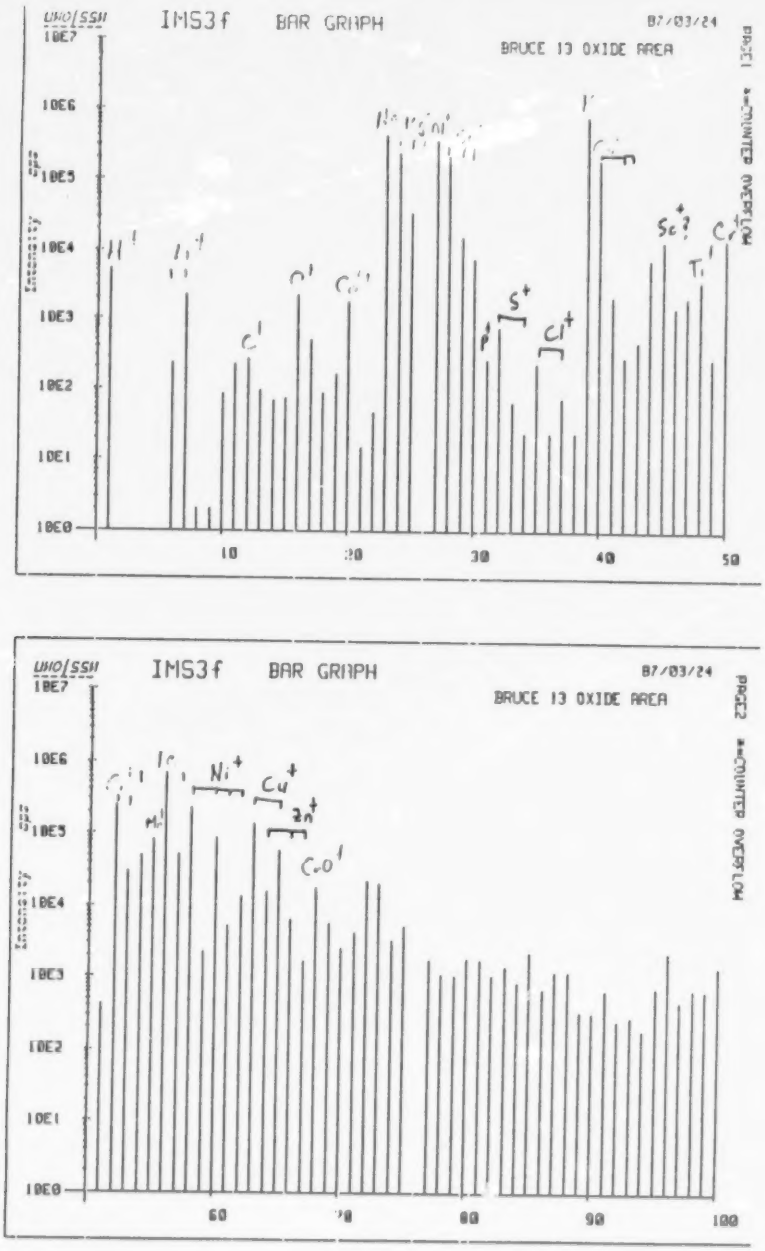
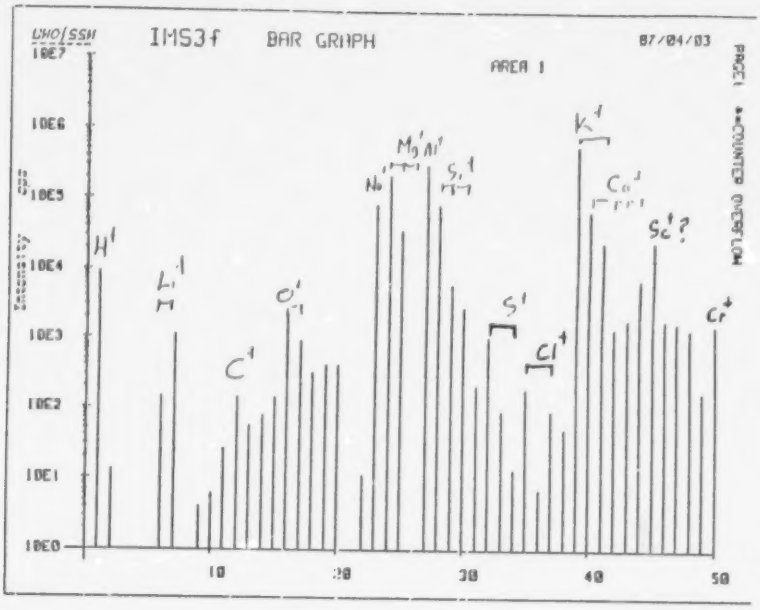


FIGURE 7.4.3

SPECIMEN C. SIMS ANALYSIS OF DEPOSIT UNDER SLUDGE PILE



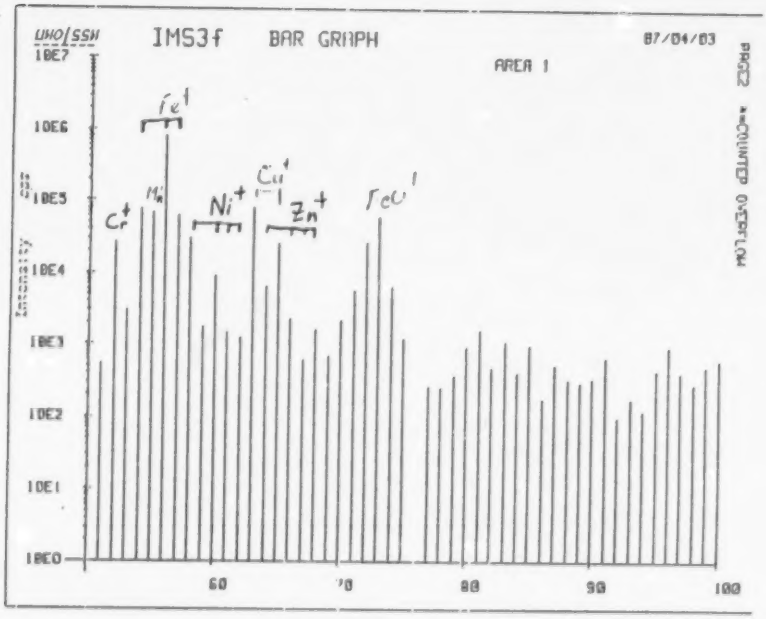
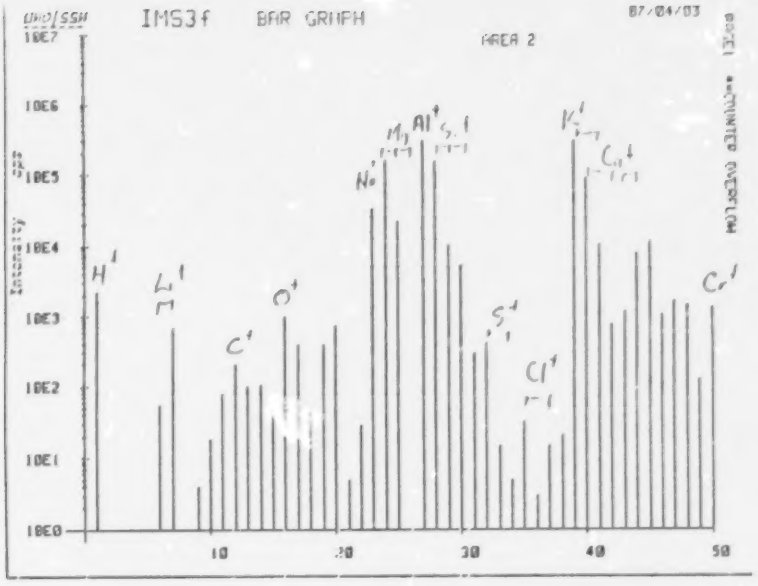


FIGURE 7.4.4.

SPECIMEN H. SIMS ANALYSIS OF
THICK DEPOSIT OUTSIDE BLOB



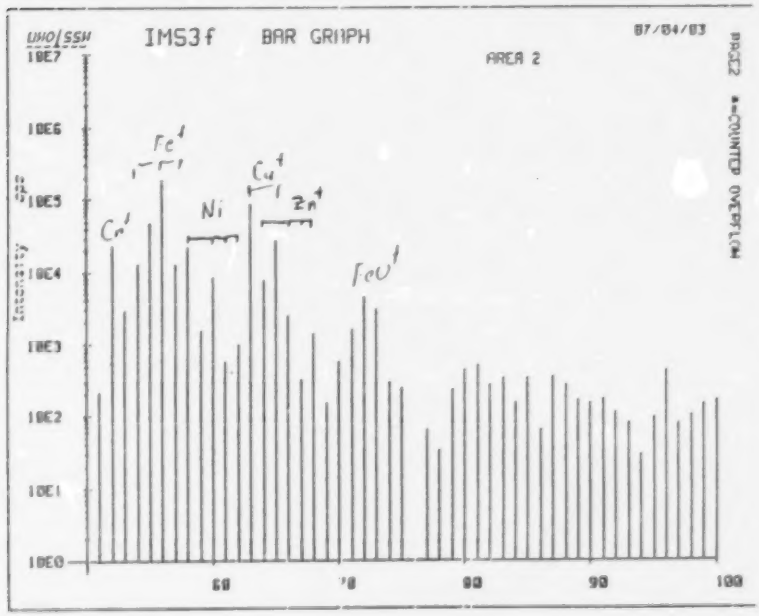
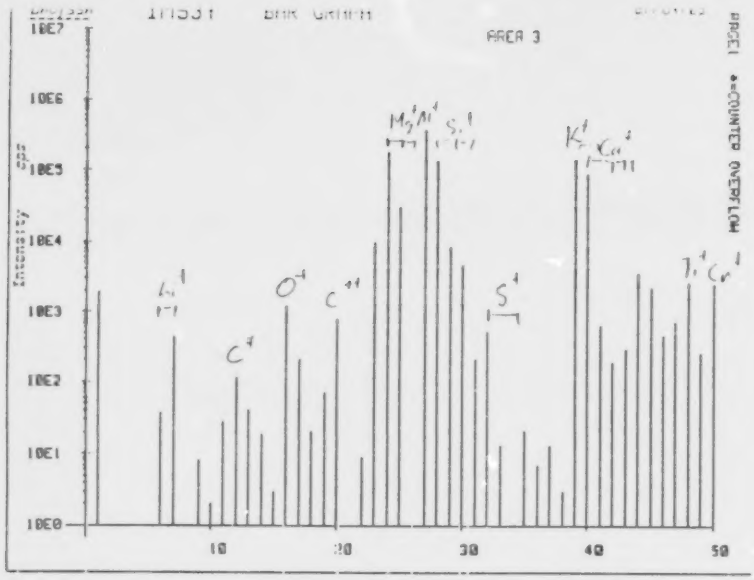


FIGURE 7.4.5

SPECIMEN H. SIMS ANALYSIS OF THICK DEPOSIT WITHIN BLOB



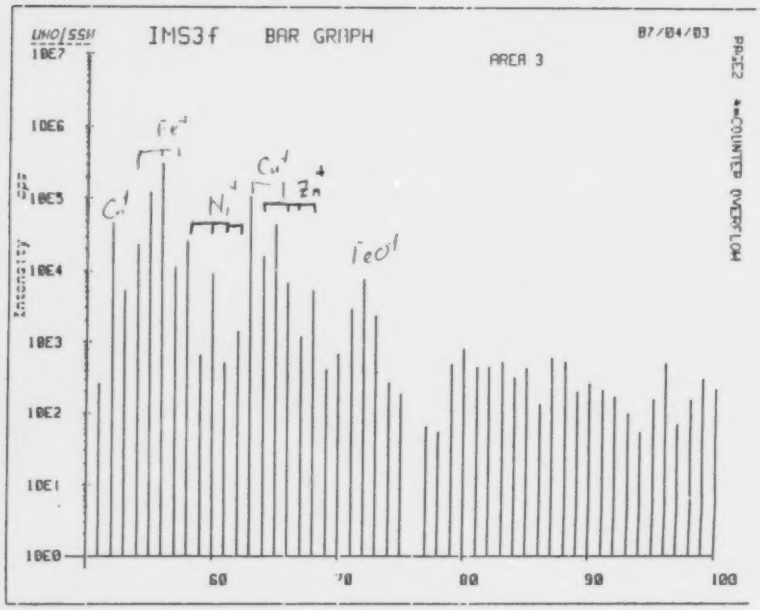


FIGURE 7.4.6

SPECIMEN H. SIMS ANALYSIS OF UNDERLYING DEPOSIT WITHIN BLOB

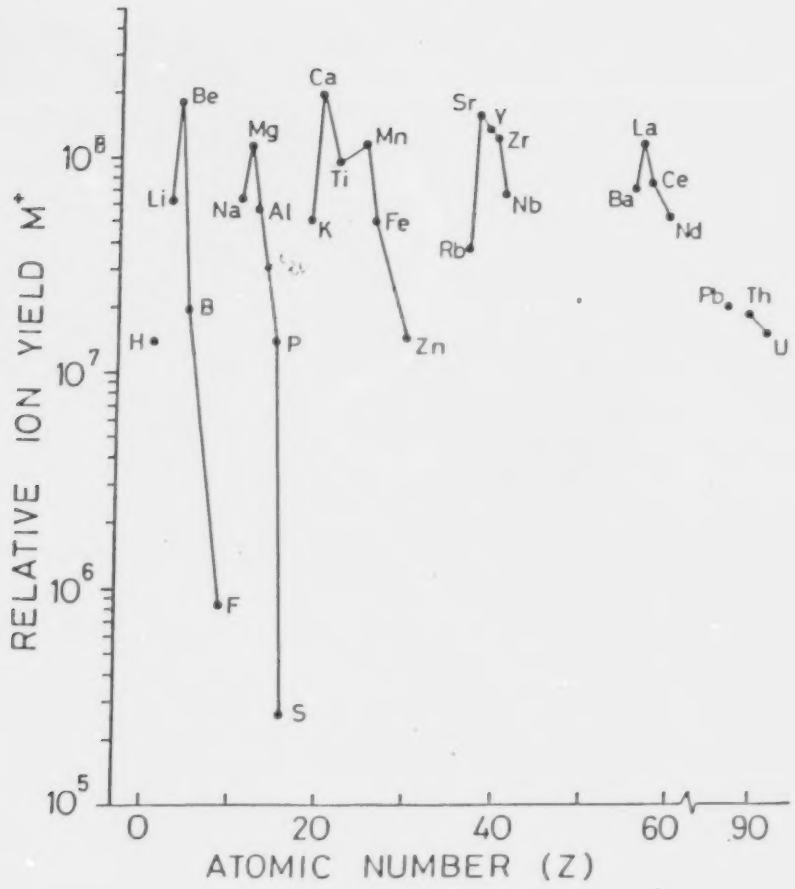


FIGURE 7.4.7

SIMS ION YIELDS FOR SOME ELEMENTS

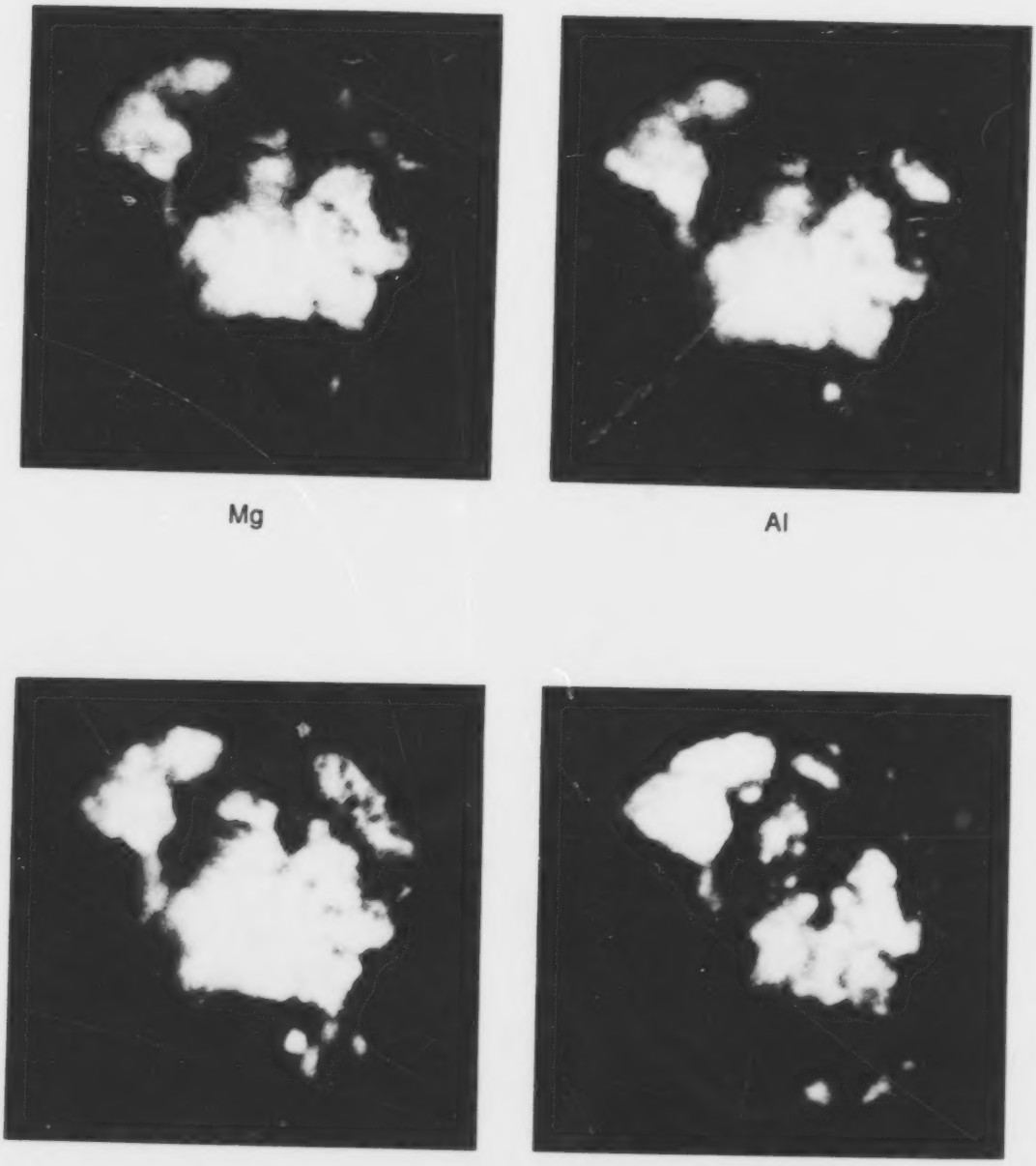


FIGURE 7.4.8

SPECIMEN H. ELEMENTAL ION IMAGES OF AREA OUTSIDE THE BLOB

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CORROSION ASSESSMENT OF TUBES REMOVED FROM BRUCE NGS UNIT 1 STEAM GENERATOR 3

P.J. King
Corrosion and Tritium Technology
Metallurgical Research

Five tubes removed from Bruce NGS unit 1 steam generator 3 in January 1987 were examined for evidence of corrosion. Superficial non-uniform corrosion to a maximum depth of 10 μm was found in the sludge pile region on all examined tubes; there was no attack above the sludge pile. The observations are consistent with degradation due to the water treatment plant sulphuric acid excursion of 1986 01 18; and suggest that a very high proportion of tubes in all Bruce NGS-A steam generators may have suffered localized corrosion to a similar extent. Attack was undetected by either eddy current or ultrasonic inspection; thus demonstrating the importance of tube removal to detect corrosion in the early stages. Non-destructive methods require further development before they can replace removal as a positive means of identifying and measuring damage.

1. INTRODUCTION

Units 1 to 4 at Bruce NGS experienced a water treatment plant acid excursion on 1986 01 18. Although the cause was remedied within 72 hours, no immediate action was taken to remove accumulated sulphuric acid from the sludge piles in the steam generators.

At the time of the incident Research Division staff identified tubing in creviced and deposit covered regions as particularly susceptible to corrosion. A range of attack morphologies was anticipated because of variable local electrochemical conditions; the list below shows those considered likely to occur.

- non-uniform wastage [similar to phosphate effects]
- pitting [this especially with chlorides and oxidizers present]
- intergranular attack

The crux of the argument was that although corrosion damage may have occurred within the period of the actual excursion, it could continue if the acid was not effectively removed from the steam generators.

Remedial action was later taken by the station based on the recommendations of Chemistry and Metallurgy staff; but only on Unit 3, which was shut down for a hot soak on 1986 01 24.

Non-destructive inspections were performed and 5 tube sections were removed from the tubesheet region of steam generator 3 during the fall 1986 outage of Unit 1 [Curcio 1986a]. Evaluations of tubing condition were carried out principally on tube R58-S42, in accordance with a plan drawn up by G. Curcio [1986b]. The investigations involved three tasks: metallurgical examination, tube deposit analyses, and corrosion assessment. This report presents the results of the corrosion assessment

2. OBJECTIVES

The purpose of the work described here was as follows.

- to examine tube surfaces for evidence of corrosion degradation
- to compare the condition of tubing at various positions
  - within the tubesheet
  - in the rolled joint
  - at the roll transition crevice and under the sludge pile
  - above the sludge pile

3. TUBE SAMPLES RECEIVED

The following tubes were received and have been examined.

Identification	Condition	Inspection notes [Curcio 1986a]
R60S43	3 large pieces + numerous small	no nde
R58S42	3 large pieces + 1 small containing part of the rolled joint	140mm sludge [ect]; defect 200mm above ts [ut]
R59S43	2 large pieces	no nde
R46S36	3 large pieces	25mm sludge [ect]; defect 100mm above ts [ut]
R69S51	many small pieces rolled joint in 2	not inspected [ect]; no defect indications [ut]

4. TUBE EXAMINATIONS

Tube examination consisted of visual examination, unaided and with a stereo microscope to x40, optical microscopy at magnifications of x50 to x200, and scanning electron microscopy at magnifications to x1000.

4.1. Visual inspection and light microscopy

Initial, unaided, visual examination of all tubes revealed their generally good condition above sludge, adherent black deposits in sludge region, and light coloured bands at the rolled-joint crevice and at the top of the sludge pile. Removal damage was evident; as well as being in many pieces, tubes were bent, scored, and otherwise variously mechanically damaged. The damage did not detract from this corrosion assessment. Further examination was carried out on selected regions of the tubes with the aid of a stereo microscope.

The following list summarizes the general observations from the initial examinations.

- Tube surfaces within the tubesheet were mostly clean and free from any corrosion. Often they showed colourations typical of heat-treated surfaces, indicating retention of the original manufactured surface condition, but occasionally there was discolouration and sparse, black crystalline deposit [magnetite] indicating a small amount of water leakage at some time.

- The rolled joints appeared to be in relatively good condition; however, there was some indication of leakage paths.
- The roll transition crevice regions had a light, metallic colour and appeared to be corroded. The severity of attack appeared to decrease in the order R58S42, R59S43, R46S36, R60S43, R69S51
- In the sludge pile region, the tubes were covered with a black, crystalline deposit which obscured most of the metal surface. The few exposed spots appeared to have suffered superficial corrosion-polishing.
- The tops of the sludge piles were delineated by a light, metallic-colour band similar to that at the roll transition crevice. These regions also appeared to be superficially corroded metal surfaces, but to a lesser extent than the crevice regions.
- Tube surfaces above the sludge were sparsely covered with a black or grey-black particulate deposit and appeared free from corrosion. Tube R58S42 had an oily appearance in this region, possibly a result of tube removal.
- The top of tube R58S42 was covered with a thick, green-brown deposit with an unusual mixed crystalline and amorphous appearance.
- The small regions of mechanical damage, that were likely responsible for the ultrasonic inspection signal, were apparent above the sludge pile on tube R46S36; however, thorough OD examination of tube R58S42 failed to reveal the source of its ultrasonic indication.

Light microscopy confirmed apparent surface degradation and provided a maximum depth measurement by refocussing of ≈10 μm on tube R58S42. Based on measurements on all tubes [10,9,7,7,5 μm] the 95% confidence limits for the depth of attack are 0 and 15 μm. Considering the effect of deposits on the measurements, the deepest attack could approach 20 μm.

4.2. Scanning electron microscopy

According to the overall examination plan [G. Curcio 1986b] only specimen 1a of tube R58S42, sample B was examined further. Scanning electron microscopy provided additional detail of attacked and deposit covered surfaces, confirming and building on the initial observations. After a first look at mechanically cleaned samples [loosely adherent deposits removed by rubbing with a plastic eraser], samples were chemically cleaned using the APAC procedure and re-examined to reveal the surface condition under adherent deposits. The following items summarize the sem observations; numbers in parentheses refer to illustrative figures.

- the good condition of the rolled joints was confirmed; original roll markings were visible even though removal through the tubesheet had caused the expected deep axial scratches {1,2}
- intergranular attack and some general dissolution produced wide grain boundary grooves to about one-half grain depth at the tube-tubesheet crevice region {1,2}
- attack is non-uniform general corrosion confined to the sludge region {3,4,5,6,7}
- circumferential grinding marks are obscured {2,3,5}
- re-examination after chemical cleaning showed that attack was not confined to top and bottom bands, but extended throughout the sludge area

4.3 Re-examination of tube R40S45, BNGS U3 SG3

The original report [Bellamy 1985] on the examination of this tube [removed 1984 11 03] indicated that it was in excellent condition, with no evidence of corrosion. The documentation included metallographic cross sections but no scanning electron micrographs of the tube surface. For purposes of comparison the archived tube samples were retrieved and re-examined in light of the corrosion observed on the tubes of this investigation. The re-examination revealed that the surface of the Unit 3 tube within the crevice region [Figure 8] is essentially the same as that of tube R58S42 above the sludge pile [Figure 7].

5. DAMAGE ASSESSMENT

5.1. Extent within steam generator

The extent of corrosion can be considered to have three main components.

- depth
- surface area
- degree of distribution

In terms of depth, the observed attack is superficial only. At a maximum measured depth of 10 µm, the attack penetrates scarcely 1% of tube wall thickness. Depth appears to vary with sludge height, but this is a qualitative observation only; even so, the relation is consistent with expectation. Since the tube examined is from the deepest sludge region, it represents one of those most severely attacked Natural, random variations in severity of corrosion mean that the 10 µm measured cannot be taken as the absolute maximum depth; rather, it is an estimate only.

In terms of surface area, the attack is extensive. The surface dimensions are thousands of times larger than the depth. On the tubes examined,the total area affected is roughly the total occluded area.

In terms of distribution, the attack is localized to crevice regions on the tubes examined, but could be distributed throughout the steam generator in other crevice regions. The sludge pile forms a large crevice site; however, other crevices within the steam generator include: scales and deposits on tube surfaces above the sludge pile, and tube to tube support plate intersections, in decreasing order of significance.

Wide and deep grain boundary grooving appeared to be confined to the roll-transition crevice area only. This may indicate a stress-assisted intergranular attack mechanism at this location. The action of the stress is to localize attack to grain boundaries in general.

It is possible that with natural variations in the sludge pile and the crevices it forms with the tubes, only a fraction of tubes are corroded throughout the sludge pile. Using the cumulative binomial probability distribution for 5 observations of corrosion in a sample size of 5, the 95% confidence limit indicates that at least 55% of susceptible tubes are attacked. With the observation of attack even with a very small sludge height, it must be presumed that all steam generator tubes are **susceptible**, and based on $\#attacked/\#examined = 1$ there is a significant probability that a very high proportion are affected to some degree.

5.2. Cause

The observed degradation is a result of either normal operation or the acid excursion of early 1986.

The only clues to the cause are the morphological features of the attack and the condition of the Bruce unit 3 steam generator tube removed from the tubesheet region in 1984. The morphological features are summarized below.

- shallow, non-uniform corrosion
- regions of polishing and etching, suggesting the presence during corrosion of a film of concentrated solution at the metal surface
- intergranular attack
- general lack of crystallographic facets that would be more typical of active dissolution in the absence of a solution film

The observations presented here are consistent with sulphuric acid attack of alloy N06600. The morphology of corrosion in concentrated sulphuric acid can range from uniform polishing to etching depending on electrochemical conditions; indeed, this principle is employed in electropolishing and electrolytic etching for metallographic specimen preparation. Similar attack has been reported in laboratory testing [Tapping et al 1986, Kendig and Isaacs 1981], and sulphuric acid has been implicated in incidences of corrosion in operating steam generators [Green and Paine 1981, Paine et al 1987].

Other environments could also be responsible: lakewater or sodium silicate [King and Dautovich 1981]. These types of environments are possible during operation [Hay and King 1982].

The most probable cause is the acid excursion; because of both the observed morphology of attack and the unattacked condition of the unit 3 tube removed in 1984.

5.3. Rate and Continuation of Growth

For the purposes of this section it is assumed that attack was caused by the acid excursion.

A number of assumptions have to be made in order to estimate the rate of degradation. Since the cause is not absolutely known, an initiation period cannot be ascertained but must be extracted from circumstantial evidence. Details of, and changes in, propagation behaviour are unavailable from the examination and must be similarly proposed from circumstances. Having made appropriate assumptions for estimating rate, predictions for continued growth can be made.

From the preceding discussion, it will be assumed that attack requires specific aggressive conditions and initiated with the water treatment plant acid excursion of 18 January 1986. Since no corrective measures were taken for this unit, it is further presumed that the aggressive conditions remained until the next unit shutdown, starting November 1986; this gives a growth period of about 10 months. It follows that the maximum observed degradation rate is 1% of wall thickness per year [using the 95% confidence limit for depth yields a rate of 1.5% per year].

Attack will not continue if the aggressive conditions are removed. Measures such as a hot soak or an extended shutdown and boiler water purification are believed to be sufficient to

remove contaminants and aggressive crevice conditions. Since the shutdown on unit 1 lasted for about 2 months, it follows that aggressive conditions were likely removed from this unit and that attack will not now be propagating due to the acid excursion.

6. IMPLICATIONS of DAMAGE

6.1. Integrity

Steam generator integrity is not immediately compromised by the degree of attack observed. General corrosion [uniform or non uniform] reduces mechanical strength in proportion to the reduction in cross-sectional area; thus, a 1% strength loss is indicated. This should be well accommodated by design margins and safety factors.

If the observed attack is the result of the acid excursion, then by itself it is not a potential integrity concern since, as already stated, no further propagation will occur from the original cause

If however it is the result of normal operation, then propagation will continue when crevice conditions are reestablished after return to power. Because of the continued presence of the sludge pile and other tube deposits, aggressive crevice conditions could reform in as little as a few months operation. This continued degradation would pose a threat to tube integrity in the long term.

The presence of intergranular penetrations may render the tubing more susceptible to further corrosion and therefore may increase the long term threat to integrity. The severity of crevice corrosion is, among other things, dependent on the physical dimensions of the occluded region. The sludge pile, scale and deposits all form crevices; however, because of its small width intergranular attack [figure 2], may constitute a more severe crevice. With a more severe crevice, corrosion may re-initiate and propagate under less aggressive bulk [or sludge pile] conditions; therefore, the tolerance for normal impurities or chemical excursions may be reduced.

6.2. Operation

The principal implication for operation is that good water chemistry must be rigorously maintained to avoid this sort of corrosion damage. It is not only sulphate or sulphuric acid that is damaging; other chemical species can cause similar or more severe attack, including pitting, intergranular attack, and stress corrosion cracking. It should be remembered that normal makeup [or even small condenser leaks] can supply sufficient contaminant to generate aggressive conditions. A system to monitor boiler chemistry and to rapidly detect an excursion should be available on all units, and remedial action should be taken immediately in the event of a chemical excursion.

The presence of attack demonstrates clearly that the sludge pile is not protective; it is cause for concern and all attempts should be made to minimize it. Some appropriate actions to accomplish this are as follows.

- avoid chemical excursions that can contribute non-volatile solutes
- avoid condenser leaks
- minimize oxygen and optimize pH to prevent piping corrosion
- minimize corrosion product transport

6.3. Other steam generators and other reactor units

It is expected that all remaining Unit 1 steam generators have suffered similar degradation. All have sludge piles and were subjected to the same bulk chemical conditions; therefore, aggressive conditions would have formed as they did in the examined steam generator.

Also it is expected that steam generators of the other 3 units of Bruce A station have suffered attack. This attack may be more or less severe because of the variable amounts of sludge and the recorded differences in the chemical excursion on each unit.

6.4. Inspection

Since both eddy current and ultrasonic techniques failed to detect the observed corrosion, it is obvious that our present non-destructive inspection capability is inadequate to determine the consequences of a chemical excursion on tube degradation when degradation is shallow, though extensive in surface area.

Early detection of attack is necessary to establish the need for remedial action. At present, this requires tube removal and destructive examination. A regular program of tube removals would be appropriate to monitor their condition. Such a program would involve some radiation exposure, cost, and reduction in heat transfer capacity of the steam generator; but, without it there is greater risk of forced outages and a shorter lead time for major repairs or remedial measures.

Improvements in non-destructive techniques could permit assessment of this type of damage with confidence, and without the need for tube removals. Research would be required to improve the ability of ultrasonics to discriminate superficial attack and to develop a reliable sizing capability. A sufficient capability must be demonstrated before ultrasonics can replace tube removal as a positive means of identifying and measuring damage.

7. CONCLUSIONS

1] Statistically, at a 95% confidence level, at least 55% of the tubes in Bruce NGS Unit 1, steam generator 3 have suffered superficial non-uniform corrosion within the sludge pile region. Indeed, there is a significant probability that a very high proportion of tubes have been attacked to some extent.

2] The attack was caused by the water treatment plant acid excursion of January 1986, with propagation until November 1986 .

3] The attack will not propagate further from the original cause due to the de-concentration of chemicals during shutdown.

4] The sludge pile is non-protective; it and other crevice forming deposits pose a substantial danger to tubing integrity.

5] Steam generators of the other 3 units of Bruce A station are likely to have suffered attack. This attack may be more or less severe than that observed for unit 1.

6] Non-destructive inspection is unable to detect corrosion in its early stages.

7] A program of tube removal is required to monitor the condition of steam generator tubes.

8. RECOMMENDATIONS

1] It is essential to include tube removal in future steam generator inspections for the following reasons.

   a] The tube examinations reported here reveal definite corrosion damage in the early stages.

   b] Non-destructive techniques are not sufficiently developed to detect the observed corrosion. The attack was entirely undetected by either eddy current or ultrasonic inspection.

   c] We need to know if other units are similarly affected - and whether to a greater or lesser extent. This cannot be done with non-destructive methods, as noted above.

   d] We have only very little data and estimates of propagation are very crude. The estimate given here of 1 to 1.5% of tube wall thickness per year is strongly dependent on the correct identification of the cause and especially on the estimated propagation time.

2] Ultrasonic or eddy current methods should be developed for improved detectability of very shallow attack, discrimination of attack morphology, and quantification of dimensions.

9. ACKNOWLEDGEMENTS

I would like to acknowledge Mr. F. W. Smith for performing the scanning electron microscopy and providing capable assistance in the other metallographic tasks. I would also like to thank staff in the Corrosion Chemistry and Decontamination Project for chemical cleaning of tube surfaces.

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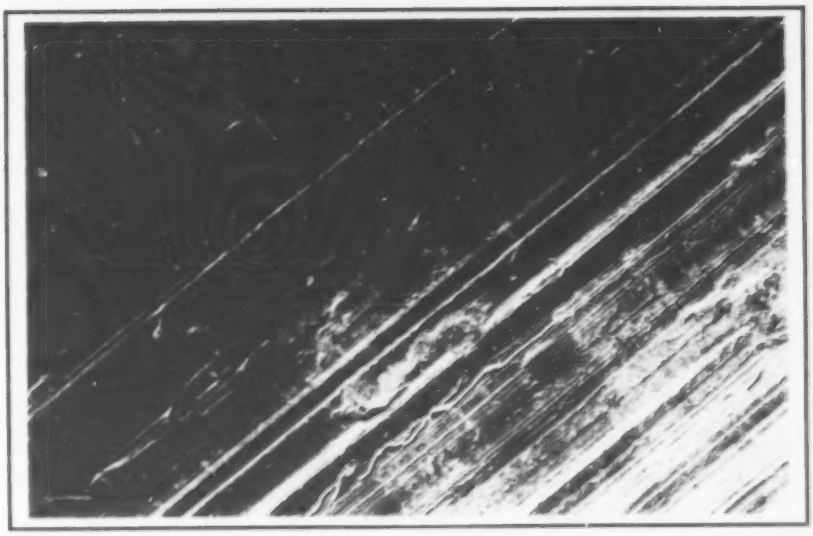
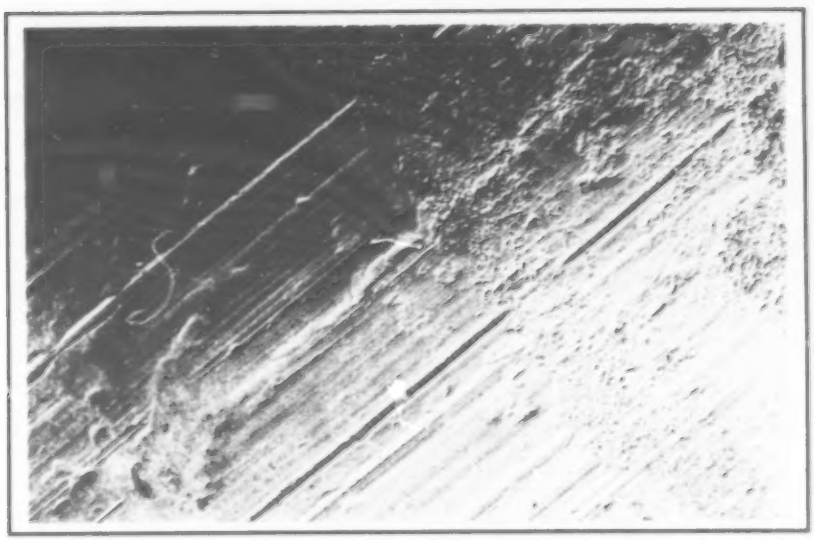
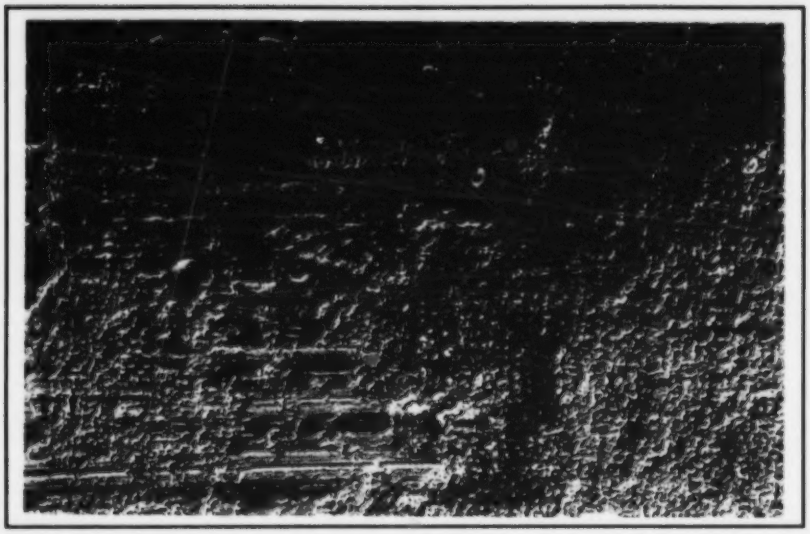


a] Within the roll proper. The removal process has produced axial score marks but roll markings in the circumferential direction are still apparent. This was typical of rolled joint condition on all tubes.



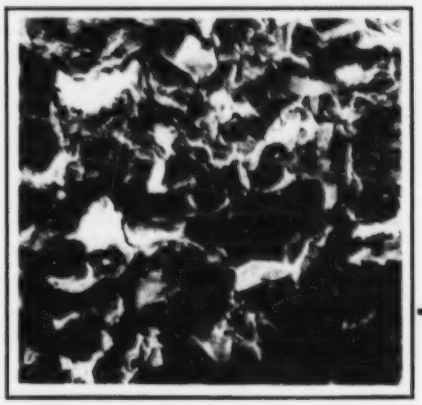
b] At the top roll transition where a crevice is formed between tube and tubesheet. The upper right of the photograph shows crevice corrosion of the tubing and the abrupt transition from a region of no attack within the rolled joint. See figure 2 for more detail.

Figure 1: Micrographs of the rolled joint region of Bruce Unit 1, SG 3 tube R58S42 after cleaning. The axis of the tube rises from left to right.



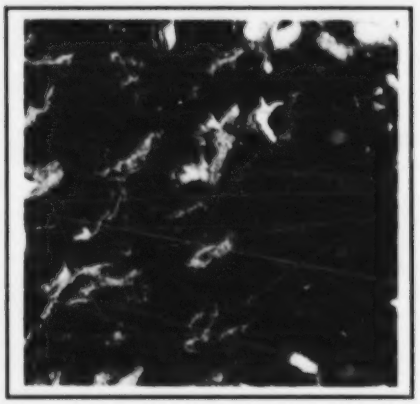
200 µm

a] Low magnification showing removal damage (axial scratches) in the roll region and the granular appearance of the crevice region. After cleaning.



25 µm

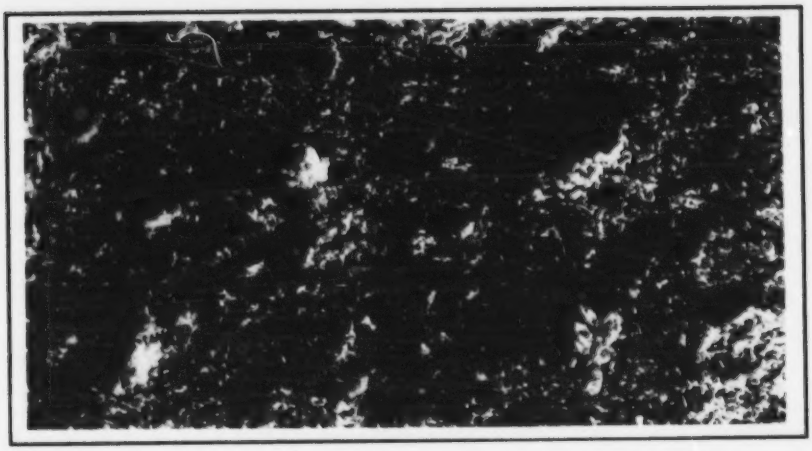
b] Higher magnification showing detail of the granular surface and presence of deposits partially obscuring the surface. Before cleaning.



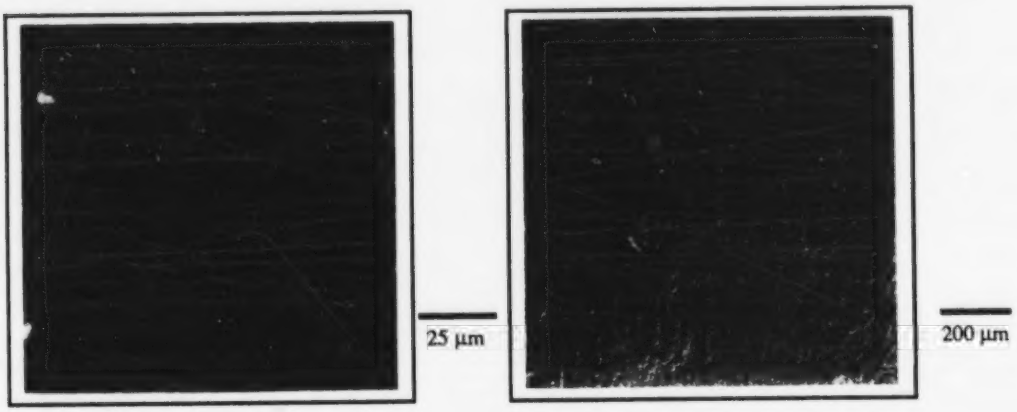
25 µm

c] As b] but after cleaning has revealed the full extent of the attack. Individual grains stand out prominently in the lower right of the photograph. Intergranular attack and some general dissolution has produced wide grain boundary grooves to about one-half grain depth.

Figure 2: Micrographs of the top roll transition and tube-tubesheet crevice region of Bruce Unit 1, SG 3 tube R58S42. The axis of the tube is from left to right. The most severe attack occurred in this region of the tube.



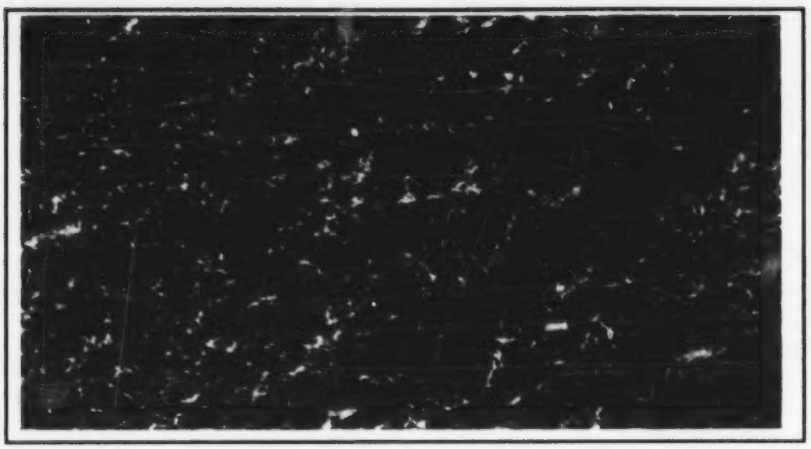
a] Before cleaning showing generally rough deposits obscuring the metal surface.



b] Metal surface after cleaning showing shallow tube damage and lack of circumferential grinding marks [compare with figures 6 & 7]. On the right side non-uniform corrosion has produced grains with a polished appearance outlined by shallow grooving On the left side, striations have resulted from corrosion-etching in certain crystallographic directions. A small amount of deposit remains at the far left of the photograph.

c] As b] but at a lower magnification showing the overall non-uniform corrosion under the sludge pile. Vertical striations in this photograph are traces of the circumferential grinding marks, nearly removed through corrosion [compare with figure 6]. This is typical of the superficial attack in this region.

Figure 3: Micrographs of deposits and tube surfaces within the lower part of the sludge pile of Bruce Unit 1, SG 3 tube R58S42. The axis of the tube is from left to right.



25 µm

a] Before cleaning. Although deposit covered, some areas of corrosion-polishing show as smooth surfaces in the centre of the photograph.

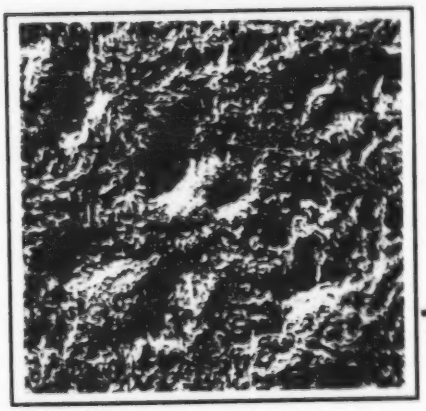
25 µm

b] After cleaning. Some deposit remains in the upper centre of the photograph, but metal surface elsewhere shows corrosion-polishing and corrosion-etching similar to that seen lower in the sludge pile.

Figure 4: Micrographs of deposits and tube surfaces within the upper part of the sludge pile of Bruce Unit 1, SG 3 tube R58S42. The axis of the tube is from left to right.

200 µm

a] The region is shown at low magnification to illustrate the transition from within the sludge to above it. The light grey area in the upper left comprising most of the photograph is just within the sludge pile; this region appeared visually as a brightened band. Note the lack of definition of circumferential grinding marks. In the lower right, grinding marks are better defined; this region is out of the sludge pile. The dark band separating the two regions is adherent scale or deposit.



25 µm

b] Detail from within the upper left region of a] showing corrosion-etched surface similar to that deeper in the sludge pile, but slightly more severe.

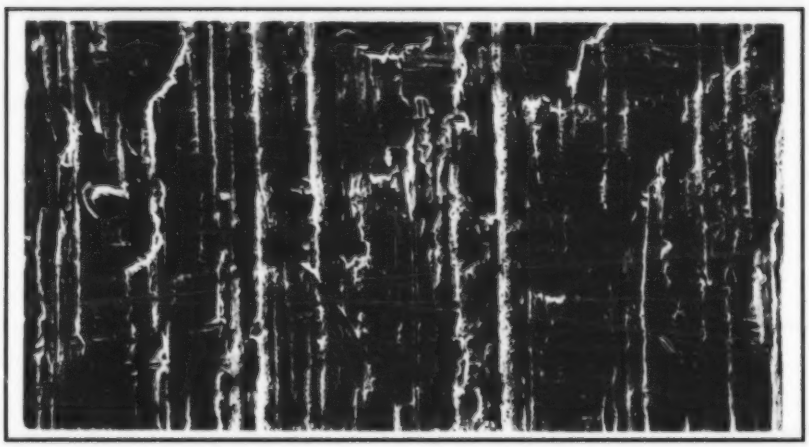
25 µm

c] Detail from within the dark band in a] showing the cracked, partially removed scale layer and the underlying corroded metal surface. The exposed metal has a dimpled surface similar to that resulting from an acid picking operation.

Figure 5: Micrographs of deposits and tube surfaces at the top of the sludge pile of Bruce Unit 1, SG 3 tube R58S42 after cleaning. The axis of the tube is from left to right.

200 µm

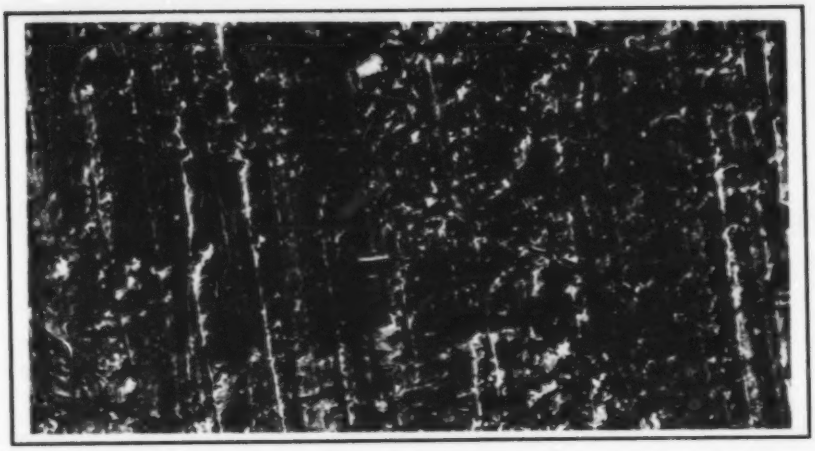
a] At low magnification showing in the upper half the continuation of the dark band shown in figure 5 a], and in the lower half a region clear of the sludge pile. [The dark band was continuous around the circumference of the tube in a sloping plane.]



25 µm

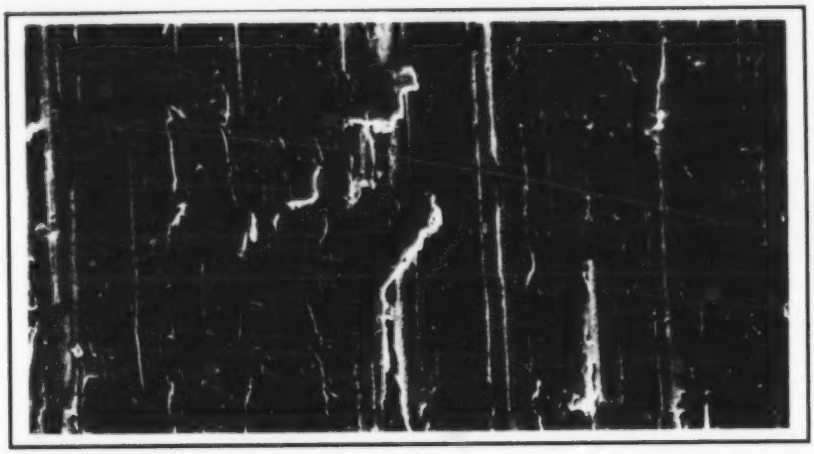
b] Detail of the lower region of a] showing a mostly clean metal surface with retained grinding marks. Some minor dimpling is apparent indicating that this area had been covered by patchy deposits.

Figure 6: Micrographs of deposits and tube surfaces just above the sludge pile of Bruce Unit 1, SG 3 tube R58S42 after cleaning. The axis of the tube is from left to right.



25 µm

a] Before cleaning the metal surface is clearly indicated by the grinding marks, but a light particulate deposit blurs the features.



25 µm

b] After cleaning features are sharpened, showing a well preserved tube surface [contrast with previous figures]. Close examination will reveal almost imperceptible dimpling showing that even the light deposit covering shown in a] can lead to localized corrosion. However, such attack is inconsequential.

Figure 7: Micrographs of the free tube surface above the sludge pile of Bruce Unit 1, SG 3 tube R58S42. The axis of the tube is from left to right.

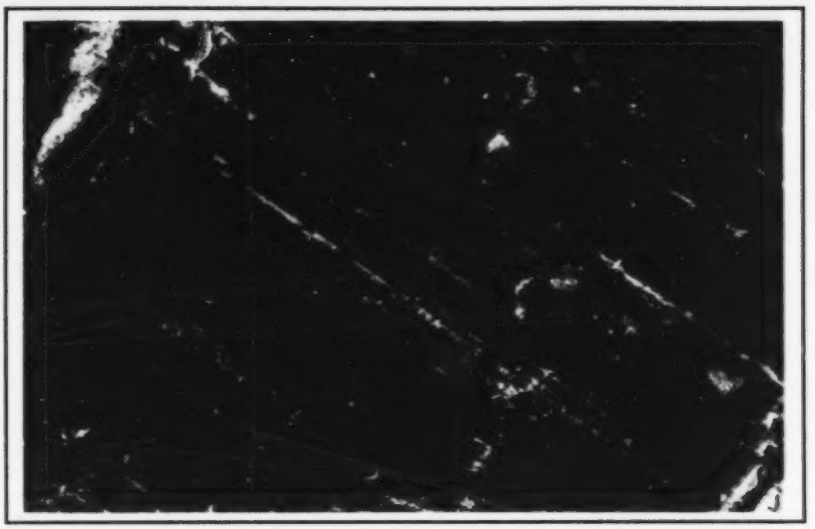


Figure 8: Micrograph of the crevice region of BNGS Unit 3 SG 3, tube R40S45 showing a well preserved tube surface and clearly visible grinding marks. The axis of the tube rises from left to right with the rolled joint on the left. Compare this with Figure 7 b].

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